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ANNUAL REPORTS
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PROGRESS OF CHEMISTRY

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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1921.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>A.</i>	Abstracts in Journal of the Chemical Society.*
<i>Acta Med. Scandinav.</i>	Acta Medica Scandinavica.
<i>Amer. Chem. J.</i>	American Chemical Journal.
<i>Amer. J. Bot.</i>	American Journal of Botany.
<i>Amer. J. Physiol.</i>	American Journal of Physiology.
<i>Amer. J. Sci.</i>	American Journal of Science.
<i>Anal. Fis. Quim.</i>	Anales de la Sociedad Española Física y Química.
<i>Analyst</i>	The Analyst.
<i>Annalen</i>	Justus Liebig's Annalen der Chemie.
<i>Ann. Bot.</i>	Annals of Botany.
<i>Ann. Chim. anal.</i>	Annales de Chimie analytique appliquée à l'Industries à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Falsif.</i>	Annales des Falsifications.
<i>Ann. Inst. Pasteur</i>	Annales de l'Institut Pasteur.
<i>Ann. Physik</i>	Annalen der Physik.
<i>Ann. Report</i>	Annual Reports of the Chemical Society.
<i>Ann. Sci. Agron.</i>	Annales de la science agronomique française et étrangère.
<i>Ann. sci. Univ. Jassy.</i>	Annales scientifiques de l'Université de Jassy.
<i>Apoth. Ztg.</i>	Apotheker-Zeitung.
<i>Arch. exp. Path. Pharm.</i> . . .	Archiv für experimentelle Pathologie und Pharma- kologie.
<i>Arch. Farm. sperim. Sci.</i> . . .	Archivio di Farmacologia sperimentale e Scienze affini.
<i>Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Arch. Schiffs u. Tropenhygiene</i> .	Archiv Schiffs- und Tropen-Hygiene.
<i>Arkiv. Kem. Min. Geol.</i>	Arkiv för Kemi, Mineralogi och Geologi.
<i>Astrophys. J.</i>	Astrophysical Journal.
<i>Atti R. Accad. Lincei</i>	Atti della Reale Accademia dei Lincei.
<i>Beibl. Ann. Phys.</i>	Beiblätter zu den Annalen der Physik.
<i>Ber.</i>	Berichte der Deutschen Chemischen Gesellschaft.
<i>Ber. Deut. bot. Ges.</i>	Berichte der Deutschen botanischen Gesellschaft.
<i>Ber. Deut. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesell- schaft.
<i>Berl. Klin. Wochenschr.</i>	Berliner Klinische Wochenschrift.
<i>Biochem. J.</i>	The Biochemical Journal.
<i>Biochem. Z.</i>	Biochemische Zeitschrift.
<i>Brennstoff-Chem.</i>	Brennstoff Chemie.
<i>Brit. Med. J.</i>	British Medical Journal.
<i>Brit. Pat.</i>	British Patent.
<i>Bul. Soc. Chim. România</i>	Buletinul Societății de Chimie din România.
<i>Bull. Acad. roy. Belg.</i>	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Jard. bot. Buitenzorg.</i> . .	Bulletin du Jardin botanique de Buitenzorg.
<i>Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>Bull. Soc. chim. Belg.</i>	Bulletin de la Société chimique de Belgique.

* The year is not inserted in references to 1921.

viii TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>Bull. Soc. chim. Biol.</i>	Bulletin de la Société de Chimie biologique.
<i>Bull. Soc. Ind. Mulhouse</i>	Bulletin de la Société Industrielle de Mulhouse.
<i>Canadian Chem. J.</i>	Canadian Chemical Journal.
<i>Centr. Bakt. Par.</i>	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
<i>Chem. Listy</i>	Chemické Listy pro vědu a průmysl.
<i>Chem. and Met. Eng.</i>	Chemical and Metallurgical Engineering.
<i>Chem. News</i>	Chemical News.
<i>Chem. Weekblad</i>	Chemisch Weekblad.
<i>Chem. Ztg.</i>	Chemiker Zeitung.
<i>Chem. Zentr.</i>	Chemisches Zentralblatt.
<i>Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>D. R.-P.</i>	Deutsches Reichs-Patent.
<i>Deutsch. Gart. Ztg.</i>	Deutsche Garten-Zeitung.
<i>Eng. and Min. J.</i>	Engineering and Mining Journal.
<i>Fermentforsch.</i>	Fermentforschung.
<i>Gazzetta</i>	Gazzetta chimica italiana.
<i>Ges. Abhandl. Kennt. Kohle</i>	Gesammelte Abhandlungen zur Kenntnis der Kohle.
<i>Giorn. Chim. Ind. Appl.</i>	Giornale di Chimica Industriale ed Applicata.
<i>Helv. Chim. Acta</i>	Helvetica Chimica Acta.
<i>Int. Z. Metal.</i>	Internationale Zeitschrift für Metallographie.
<i>Jahrb. Min.</i>	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
<i>Jap. Pat.</i>	Japanese Patent.
<i>J. Agric. Res.</i>	Journal of Agricultural Research.
<i>J. Agric. Sci.</i>	Journal of Agricultural Science.
<i>J. Amer. Chem. Soc.</i>	Journal of the American Chemical Society.
<i>J. Biol. Chem.</i>	Journal of Biological Chemistry.
<i>J. Chem. Ind. Japan (or Tokyo)</i>	Journal of Chemical Industry, Japan.
<i>J. Chem. Met. Soc. S. Africa</i>	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
<i>J. Chim. phys.</i>	Journal de Chimie physique.
<i>J. Coll. Eng. Tokyo</i>	Journal of the College of Engineering, University of Tokyo.
<i>J. Coll. Sci. Tokyo</i>	Journal of the College of Science, Imperial University of Tokyo.
<i>J. Franklin Inst.</i>	Journal of the Franklin Institute.
<i>J. Gen. Physiol.</i>	Journal of General Physiology.
<i>J. Ind. Eng. Chem.</i>	Journal of Industrial and Engineering Chemistry.
<i>J. Landw.</i>	Journal für Landwirtschaft.
<i>J. Min. Agric.</i>	Journal of the Ministry of Agriculture.
<i>J. Pharm. Chim.</i>	Journal de Pharmacie et de Chimie.
<i>J. Pharm. Soc. Japan.</i>	Journal of the Pharmaceutical Society of Japan.
<i>J. Physical Chem.</i>	Journal of Physical Chemistry.
<i>J. Physiol.</i>	Journal of Physiology.
<i>J. pr. Chem.</i>	Journal für praktische Chemie.
<i>J. Roy. Hort. Soc.</i>	Journal of the Royal Horticultural Society.
<i>J. Roy. Soc. New South Wales</i>	Journal and Proceedings of the Royal Society of New South Wales.
<i>J. S. African Assoc. Anal. Chem.</i>	Journal of the South African Association of Analytical Chemists.
<i>J. Soc. Chem. Ind.</i>	Journal of the Society of Chemical Industry.
<i>J. Soc. Dyers and Col.</i>	Journal of the Society of Dyers and Colourists.
<i>J. Tokyo Chem. Soc.</i>	Journal of the Tokyo Chemical Society.
<i>J. Washington Acad. Sci.</i>	Journal of the Washington Academy of Sciences.
<i>Koll. Chem. Beihefte</i>	Kolloidchemische Beihefte.
<i>Kolloid Z.</i>	Kolloid Zeitschrift.
<i>Landw. Jahrb.</i>	Landwirtschaftliche Jahrbücher.
<i>Landw. Versuchs-Stat.</i>	Die Landwirtschaftlichen Versuchs-Stationen.

TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES. ix

ABBREVIATED TITLE.	JOURNAL.
<i>Medd. K. Vetenskapsakad.</i>	Meddelanden från Kongl-Vetenskapsakademiens
<i>Nobel-Inst.</i>	Nobel-Institut.
<i>Mem. Coll. Sci. Kyōtō</i>	Memoirs of the College of Science, Kyōtō Imperial University.
<i>Mcm. Manchester Phil. Soc.</i>	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
<i>Metall u. Erz</i>	Metall und Erz.
<i>Min. Mag.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i>	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Nuovo Cim.</i>	Il Nuovo Cimento.
<i>Öfvers. Finska Vet.-Soc.</i>	Öfversigt af Finska Vetenskaps-Societetens Förhandlingar, Helsingfors.
<i>Perf. and Essent. Oil. Rec.</i>	Perfumery and Essential Oil Record.
<i>Pflüger's Archiv</i>	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. J.</i>	Pharmaceutical Journal.
<i>Pharm. Weekblad</i>	Pharmaceutisch Weekblad.
<i>Pharm. Zentr.-h.</i>	Pharmazeutische Zentralhalle.
<i>Phillipine J. Sci.</i>	Phillipine Journal of Science.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society of London.
<i>Physical Rev.</i>	Physical Review.
<i>Physikal. Z.</i>	Physikalische Zeitschrift.
<i>Physiol. Abstr.</i>	Physiological Abstracts.
<i>Proc. Cam. Phil. Soc.</i>	Proceedings of the Cambridge Philosophical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Nat. Acad. Sci.</i>	Proceedings of the National Academy of Sciences.
<i>Proc. Physical Soc.</i>	Proceedings of the Physical Society of London.
<i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i>	Proceedings of the Royal Society of Edinburgh.
<i>Rec. trav. chim.</i>	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Rev. Gén. Mat. Col.</i>	Revue Générale des Matières Colorantes.
<i>Schweiz. Apoth. Ztg.</i>	Schweizerische Apotheker Zeitung.
<i>Sitzungsber. Preuss. Akad. Wiss. Berlin</i>	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
<i>Skand. Arch. Physiol.</i>	Skandinavisches Archiv für Physiologie.
<i>Soil Sci.</i>	Soil Science.
<i>Stahl u. Eisen</i>	Stahl und Eisen.
<i>Staz. sper. agr. ital.</i>	Stazioni sperimentali agrarie italiane.
<i>Svensk. Kem. Tidskr.</i>	Svensk Kemist Tidskrift.
<i>T.</i>	Transactions of the Chemical Society.
<i>Texas Agric. Expt. Station Bull.</i>	Bulletins of the Texas Agricultural Experiment Station.
<i>Trans. Faraday Soc.</i>	Transactions of the Faraday Society.
<i>Ver. Deut. Physikal. Ges.</i>	Verhandlungen der deutschen physikalischen Gesellschaft.
<i>Z. anal. Chem.</i>	Zeitschrift für analytische Chemie.
<i>Z. angew. Chem.</i>	Zeitschrift für angewandte Chemie.
<i>Z. anorg. Chem.</i>	Zeitschrift für anorganische und allgemeine Chemie.
<i>Z. Biol.</i>	Zeitschrift für Biologie.
<i>Z. Deut. Öl Fett Ind.</i>	Zeitschrift der deutschen Öl-und Fett-Industrie.
<i>Z. Elektrochem.</i>	Zeitschrift für Elektrochemie.
<i>Z. ges. Schiess- u. Sprengstoffw.</i>	Zeitschrift für das gesammte Schiess-und Sprengstoffwesen.
<i>Z. Hyg.</i>	Zeitschrift für Hygiene und Infektionskrankheiten.

X TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>Z. Kryst. Min.</i> . . .	Zeitschrift für Krystallographie und Mineralogie.
<i>Z. Metallkunde</i> . . .	Zeitschrift für Metallkunde.
<i>Z. Nahr.-Genussm.</i> . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Z. öffentl. Chem.</i> . . .	Zeitschrift für öffentliche Chemie.
<i>Z. Physik</i>	Zeitschrift für Physik.
<i>Z. physikal. Chem.</i> . . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Z. physikal. Chem. Unterr.</i>	Zeitschrift für den physikalischen und Chemischen Unterricht.
<i>Z. physiol. Chem.</i> . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

Specific Heats.

The molecular heat of hydrogen from 0—2600° abs. has been calculated ¹ on the basis of Bohr's model of the hydrogen molecule and the assumption that the rotational energy corresponds with *three* degrees of freedom. The molecular energy of gases has been discussed ² from the point of view of dynamical theory. The increase of specific heat on rise of temperature is assumed to be due to vibrations between the atoms, to which the principle of equipartition does not apply. Equipartition of energy is assumed between each degree of freedom of translation and each effective degree of freedom of rotation. The abnormal behaviour of hydrogen at low temperatures ³ is supposed to be due to a change of molecular structure which deprives the molecule of its two degrees of freedom of rotation. In tri- and poly-atomic gases there is generally a considerable amount of energy of vibration. The conclusion is drawn that the quantum theory is unnecessary, but that the observed facts are not in conflict with it.

The specific heat of nitrogen at 92° abs., corrected for deviations from the gas laws, is almost exactly the equipartition value.⁴ The value of dC_p/dp is 0.300 cal./atm.

The velocity of sound in a dissociating gas, such as $N_2O_4 \rightleftharpoons 2NO_2$, has been calculated.⁵ It depends on the reaction velocity coefficients, and the latter may be determined in this way.

The internal energy of solids from the point of view of atomic

¹ F. H. MacDougall, *J. Amer. Chem. Soc.*, 1921, **43**, 23; *A.*, ii, 238.

² (Sir) J. A. Ewing, *Proc. Roy. Soc. Edin.*, 1920, **40**, 102; *A.*, ii, 299.

³ Eucken, *A.*, 1912, ii, 232.

⁴ R. Bartels and A. Eucken, *Z. physikal. Chem.*, 1921, **98**, 70.

⁵ A. Einstein, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, 380; compare F. Keutel, *Diss.*, Berlin, 1911.

structure has been considered.⁶ Further measurements of specific heats at low temperatures have been determined with a modified form of Nernst and Schweser's apparatus.⁷ The results are in most cases in good agreement with Debye's formula.⁸ The velocity of sound in air, nitrogen, carbon dioxide, methane, and ethane, at temperatures up to 1000° has been determined by a direct method.⁹ The true molecular heats at constant volume are calculated: air $4.8 + 0.0004T$; nitrogen $4.775 + 0.00042T$; carbon dioxide $6.30 + 0.00205T + 0.0000007T^2$; methane $6.66 + 0.019t$; ethane $9.04 + 0.0183t$.

The difference of the molecular heats of a gas has been calculated by three new equations: ¹⁰ $C_p - C_v = 0.000087/d_c v_c = 0.0935L/T' = 0.0935p_c/T_c d_c$. The symbols denote: critical density d_c , critical volume v_c , critical temperature T_c , boiling point T' , latent heat L , and the third equation is derived from the relation $L = p_c T' / T_c d_c$.¹¹ The equation of state of D. Berthelot seems, however, to be particularly adapted to such calculations,¹² except at very low temperatures.¹³

An apparatus for the measurement of the velocity of sound in small quantities of gas at different temperatures is described.¹⁴

Molecular Structure.

Several calculations of molecular diameters from the viscosities of gases have been made.¹⁵ In size and shape the atoms of monatomic inert elements are nearly indistinguishable from the atoms, respectively, of the neighbouring diatomic elements in the periodic table, the dimensions of which have been deduced indirectly from X-ray crystal measurements. A chlorine molecule may be regarded as having the size and shape of two argon atoms in contact, that is, with their external electron shells touching each other. Gaseous bromine is similarly related to double krypton atoms, and iodine to xenon. An oxygen molecule has the same size and shape as two neon atoms in contact. The shape of a molecule composed of

⁶ F. Skaupy, *Z. Physik*, 1921, **4**, 100; *A.*, ii, 300.

⁷ Paul Günther, *Ann. Physik*, 1920, [iv], **63**, 476; *A.*, ii, 16.

⁸ *A.*, 1912, ii, 1134.

⁹ H. B. Dixon, C. Campbell, and A. Parker, *Proc. Roy. Soc.*, 1921, [A], **103**, 1; *A.*, ii, 621.

¹⁰ W. Herz, *Z. Elektrochem.*, 1921, **27**, 125; *A.*, ii, 299.

¹¹ *A.*, 1919, ii, 494.

¹² Compare W. Rücker, *Ann. Physik*, 1921, **65**, 393.

¹³ Schimank, *Physik. Z.*, 1916, **17**, 393.

¹⁴ F. Himstedt and R. Widder, *Z. Physik*, 1921, **4**, 355.

¹⁵ A. O. Rankine, *Proc. Roy. Soc.*, 1921, [A], **98**, 360, 369, 331; *A.*, ii, 192, 192, 489; compare *Phil. Mag.*, 1921, [vi], **42**, 616.

two equal atoms is assumed to be a spheroid, the volume of which is equal to the sum of the volumes of the hard elastic spheres to which each participating atom is equivalent. The nitrogen molecule is equivalent to a hard, elastic body nearly spherical in shape. The close similarity between the physical properties of nitrous oxide and carbon dioxide again appears from viscosity measurements: their molecules appear to have the same size and shape, and possess an external electron arrangement practically the same as that of three neon atoms in line and contiguous. The diameter of the outer electron shell of cyanogen is nearly equal to that of bromine, as found from crystal measurements. This agrees with the equality of the molecular volumes of potassium bromide and cyanide, and with the assumptions of Lewis¹⁶ and Langmuir¹⁷ with regard to the similarity of the nitrogen and cyanogen molecules. Non-spherical molecules, built up of atoms of unequal sizes, have also been considered.¹⁸ The increases in diameter in passing from neon to ammonia, argon to phosphine, and krypton to arsine are approximately equal, and may represent the effect of the addition of the three nuclei of the hydrogen atoms added to complete the electron configuration of the corresponding inert atom. The calculations are based on Chapman's modification of Sutherland's formula: $4\pi\sigma^2 = 0.491(1 + \epsilon)\rho\bar{V}/\sqrt{2\nu\eta(1 + C/T)}$, where σ = radius of molecule; ρ = density; $\bar{V}$ = mean speed; ν = no. of molecules per c.c., η = viscosity, ϵ is practically = 0, C is a constant, T = abs. temperature.

The symmetrical shapes of polyatomic molecules assumed in such calculations as the above introduce difficulties in other departments of physical measurement, particularly in connexion with the molecular heats. This matter has been discussed¹⁹ and the formulæ of water, hydrogen sulphide, and ammonia deduced from the theory of Lewis¹⁶ assuming distortion of the octets. In water, the linking angle is approximately the same as that between carbon bonds. The distance between the oxygen nucleus and the hydrogen nuclei is the same in both cases, but is different from that between the two hydrogen nuclei. The two hydrogen atoms lie in one half of the resulting tetrahedron and two electron pairs in the other half, expressing the dipolar character of water. An asymmetric structure favours association.

The structure of molecules has also been considered²⁰ on the

¹⁶ *A.*, 1916, ii, 310.

¹⁷ *Ibid.*, 1919, ii, 328.

¹⁸ A. O. Rankine, *Proc. Physical Soc.*, 1921, **33**, 362; *A.*, ii, 584; *Phil. Mag.*, 1921, [vi], **42**, 601.

¹⁹ E. J. Cuy, *Z. Elektrochem.*, 1921, **27**, 371; *A.*, ii, 584.

²⁰ G. Kirsch, *Z. physikal. Chem.*, 1920, **96**, 471; *A.*, ii, 193.

basis of Kossel's hypothesis.²¹ The stability of the nitrogen molecule is due to the additional nucleus, and the similarity of the -CN group to halogens (see above) is due to this cause. Similar stabilising nuclei are assumed to be present in the molecules of carbon monoxide, ozone, oxides of nitrogen, and the -CNO radicle.

The cubical atom theory has been considered²² from the point of view of internal structure, and the radii of atoms have been calculated. The electronic affinities and heats of formation can also be satisfactorily found.²³

The collision between molecules and free electrons has been studied.²⁴ In the case of slow electrons (1 volt) it was found that the electron is either absorbed outright, or not in any way influenced as regards its direction and velocity by the gas molecule. For every atom or molecule there seems to be a fixed sphere of action, outside which a slow electron is not influenced, but inside which it is strongly influenced. A law of force of rapidly diminishing *continuous* distance action is regarded as improbable. Argon shows deviations, and is also peculiar in exhibiting selective absorption.

Molecular volumes have been considered²⁵ from the point of view of the Lewis-Langmuir theory, and particularly the theory of isosteres. Isosteric molecules and nuclear atoms in hydrogen compounds are shown to have the same volume. The latter depends on the number and arrangement of the electrons surrounding the nucleus rather than on the charge on the latter. Nitrogen and carbon monoxide molecules probably have a normal acetylenic structure, three pairs of electrons being shared, rather than the condensed structure suggested by Langmuir (see above).

An interesting theory of colour in relation to molecular structure has been put forward.²⁶ In some cases, an atom of large atomic volume is unable to form a stable octet by taking an electron from an atom of small atomic volume, in which the attraction between the kernel and electrons is greater. An unstable orbit, which may be disturbed by light, then results. It has been known for some time that compounds in which an atom is unsaturated, or in which

²¹ *A.*, 1916, ii, 243.

²² A. Landé, *Z. Physik*, 1920, **2**, 87; *A.*, ii, 189; *ibid.*, 380; *A.*, ii, 189; E. Madelung and A. Landé, *ibid.*, 230; *A.*, ii, 190; H. Schwendenwein, *ibid.*, 1921, **4**, 73; *A.*, ii, 310.

²³ See *Ann. Reports*, 1920.

²⁴ H. F. Mayer, *Ann. Physik*, 1921, [iv], **64**, 451; *A.*, ii, 234; C. Ramsauer, *ibid.*, 513; *A.*, ii, 324; O. Klein and S. Rosseland, *Z. Physik*, 1921, **4**, 46; *A.*, ii, 291.

²⁵ R. N. Pease, *J. Amer. Chem. Soc.*, 1921, **43**, 991; *A.*, ii, 437.

²⁶ J. Meisenheimer, *Z. physikal. Chem.*, 1921, **98**, 304; *A.*, ii, 364.

two atoms of the same element exhibit different valencies, are usually coloured.

When the atomic diameter is calculated from b of van der Waals's equation by the formula $\sigma = (3b/2\pi N)^{1/3}$, where $N = 2.75 \times 10^{19}$, the increase in passing from one inert gas to another is constant (0.28×10^{-8} cm.). This relation is not obtained when σ is calculated from the viscosities; it is in agreement with Langmuir's theory.²⁷ The atomic radii of helium, neon, argon, krypton, and xenon are supposed, on the basis of theoretical considerations,²⁸ to be in the proportion 3 : 4 : 6 : 7 : 8. The true radii of the atoms are multiples of one "elementary length," 0.036 to 0.039 Å.

An ingenious calculation of the absorption spectrum of hydrogen chloride from the quantum theory of molecular rotations²⁹ lends support to the existence of the two isotopes of chlorine.

Surface Tension.

Further investigations of thin films on water have been made.³⁰ Any further quantity of oleic acid, placed on water already covered with a layer of thickness double that which corresponds with the maximum extension, does not undergo spontaneous extension, but forms globules. The layer is then regarded as "saturated." If the surface occupied by a given quantity of oleic acid is reduced, the tension decreases and then suddenly becomes constant. An improved technique for the investigation of thin films on water has been described.³¹ The compressibility curves of the film are accurately straight lines, with a doubtful deviation at very low compressions. An abrupt change in the properties of the film takes place at an acidity of $10^{-5}N$, under compression less than 16 dynes/cm. The area occupied by each molecule becomes about 20 per cent. greater than on neutral solutions. Langmuir's view³² that the films consist of a single layer of molecules, with the carboxyl groups turned towards the water, is confirmed and extended. Different films, and even different parts of the same

²⁷ L. St. C. Broughall, *Phil. Mag.*, 1921, [vi], **41**, 872; *A.*, ii, 445.

²⁸ M. Pierucci, *Nuovo Cim.*, 1921, [vi], **22**, 189; *A.*, ii, 583; compare *A.*, 1920, ii, 538.

²⁹ A. Kratzer, *Z. Physik*, 1920, **3**, 460; *A.*, ii, 140; *ibid.*, 289; *A.*, ii, 142. Compare W. L. Bragg and H. Bell, *Nature*, March 24, 1921; *A.*, ii, 689; G. Hettner, *Z. Physik*, 1920, **1**, 345; *A.*, ii, 144; E. S. Imes, *Astrophys. J.*, 1919, **50**, 251; *A.*, ii, 4; A. Haas, *Z. Physik*, 1921, **4**, 68; *A.*, ii, 286; F. W. Loomis, *Astrophys. J.*, 1920, **52**, 248; *A.*, ii, 530.

³⁰ A. Marcelin, *Compt. rend.*, 1921, **173**, 38; *A.*, ii, 488. Compare *Ann. Physique*, 1913.

³¹ N. K. Adam, *Proc. Roy. Soc.*, 1921, [A], **99**, 336; *A.*, ii, 488.

³² *A.*, 1917, ii, 525.

film, vary considerably in their resistance to collapse on compression. The latter seems to be aided by nuclei. A mutual influence between saturated and unsaturated molecules in the same film has been detected.³³

The adhesional work, W_A , between mercury and organic liquids has been calculated³⁴ by the formula $W_A = \gamma_1 + \gamma_2 - \gamma_{12}$, where γ_1 and γ_2 are the free surface energies of the two liquids and γ_{12} the free surface energy of the interface. In some cases the latter is negative,³⁵ and the surfaces rise in temperature when they are formed. The liquids which show this abnormal behaviour in contact with water are heptinene, *n*- and *sec*.-octyl alcohols, and heptaldehyde. Addition of oxygen increases the tensile energy feebly, whilst the adhesional energy towards water is largely increased. Double bonds show the opposite effects. The facts are explained on the assumption that unsymmetrical molecules are oriented in the surface. Oxygen atoms turn towards the water. The length of a hydrocarbon chain is of more importance in determining the solubility than the nature of the active group at the end of the molecule. The triple bond has a greater relative effect on the adhesional energy than on the adhesional work at 20° as compared with a hydroxyl oxygen atom.

The surface tension of mercury in a vacuum at various temperatures has been determined by the drop method^{36, 37} and the interfacial tensions between mercury and a number of organic liquids have been found by the same method. The adhesional work between mercury and an organic liquid is always greater than between water and the liquid, or between the liquid and itself. It decreases rapidly with increase of temperature, whilst the total energy increases.

The statical measurement of interfacial tension, and the relation between interfacial tension and surface tension in organic solvents in contact with aqueous solutions have been described.³⁸

By combining Trouton's rule with the Eötvös expression, the relation $L = 20\gamma/S^{\frac{2}{3}}M^{\frac{1}{3}}$, where L = latent heat, M = molecular weight, γ = surface tension at the boiling point and S = density at the boiling point, has been deduced.³⁹ This holds approximately

³³ P. Woog, *Compt. rend.*, 1921, **173**, 387; *A.*, ii, 575.

³⁴ W. D. Harkins and E. H. Grafton, *J. Amer. Chem. Soc.*, 1920, **42**, 2534; *A.*, ii, 87.

³⁵ W. D. Harkins and Y. C. Cheng, *ibid.*, 1921, **43**, 35; *A.*, ii, 242; compare *A.*, 1920, ii, 357.

³⁶ W. D. Harkins and W. W. Ewing, *ibid.*, 1920, **42**, 2539; *A.*, ii, 87.

³⁷ J. Palacios, *Anal. Fis. Quím.*, 1920, **18**, 294; *A.*, ii, 304.

³⁸ W. C. Reynolds, *T.*, 1921, **119**, 460, 466.

³⁹ W. Herz, *Z. Elektrochem.*, 1921, **27**, 25; *A.*, ii, 300.

for normal, but not for associated, liquids. From this the molecular diameter d may be calculated by the formula $d = 1/10(M/S)^{\frac{1}{3}} \cdot 0.00102/42700$. The internal pressure is calculated by the formula $B = L/2v = 10\gamma/(Mv)^{\frac{1}{3}} \times 42700/1033$, where Mv is the molecular volume. The following values were found: benzene 1830 atm., ethyl acetate 1425 atm., aniline 2120 atm.

The latent heat may also be calculated from the critical data by the equation $L = 0.00093T_s/d_c v_c$, where T_s is the absolute boiling point, and d_c and v_c are the critical density and volume, respectively.⁴⁰ From the Trouton rule it follows that $M \times 0.00093/d_c v_c$ must be constant. This is approximately the case with normal liquids.

It has been shown⁴¹ that if the glass is properly cleaned, and evaporation of liquid prevented, the supposed finite contact angle in the measurement of the surface tensions of some organic liquids does not exist. The correction for the capillary rise in wide tubes calculated by Laplace and Rayleigh was also verified.⁴²

The effect of adsorbed gases on the surface tension of water has been found; the surface tension is diminished by an amount which is greater the higher the density of the gas, except for carbon dioxide.⁴³

The relation $1/\beta J = -2\lambda_1 s$, in which λ_1 is the internal latent heat, β the compressibility, and s the specific gravity, of a liquid, has been deduced⁴⁴ from van der Waals's equation on the assumption that a is independent of volume. If a depends on volume, $1/\beta J = \epsilon \lambda_1 s$, where $\epsilon = \rho/\alpha$ and $\rho = 1/\sigma \cdot \partial\sigma/\partial T$, the coefficient of variation of surface energy σ with temperature; $\alpha = 1/v \cdot \partial v/\partial T$. The first equation is approached at higher temperatures, the second at lower temperatures. J is the mechanical equivalent of heat.

The equation $MLJ = \pi\gamma d^2 N + RT$, where d is the molecular diameter, γ the surface tension, and N Avogadro's number, has been deduced⁴⁵ for the latent heat of evaporation. The values of d calculated agree with those found by Bragg, or from kinetic theory. Vaporisation is considered as a discontinuous change, the elementary quantity of energy concerned being $10 \times 10^{-16} T$ ergs. The value of K in $\pi\gamma d^2 N = K(T_c - T)$ agrees with that from Eötvös's law. The connexion between Trouton's rule and Wien's

⁴⁰ W. Herz, *Z. Elektrochem.*, 1921, **27**, 26; *A.*, ii, 300; compare *A.*, 1919, ii, 494.

⁴¹ T. W. Richards and E. C. Carver, *J. Amer. Chem. Soc.*, 1921, **43**, 827; *A.*, ii, 384; compare *A.*, 1915, ii, 522.

⁴² Compare also S. Sugden, *T.*, 1921, **119**, 1483.

⁴³ S. S. Bhatnagar, *J. Physical Chem.*, 1920, **24**, 716; *A.*, ii, 169; compare also reference ⁴¹.

⁴⁴ D. L. Hammick, *Phil. Mag.*, 1921, [vi], **41**, 21; *A.*, ii, 84; compare Lewis, *Z. physikal. Chem.*, 1911, **78**, 24.

⁴⁵ R. Audubert, *Compt. rend.*, 1921, **172**, 375; *A.*, ii, 240.

displacement law, $\lambda_m T = \text{const.}$, has also been pointed out.⁴⁶ The latent heat of evaporation is given by $L = Nh\nu$, where h is Planck's constant, and ν a frequency, but the critical energy increment is an average value. The formula is obtained as follows: $\lambda_m T_c = 0.28986$; $\nu = c/\lambda_m$ (c = velocity of light); hence $L = Nh\nu = Nh c T_c / 0.28986 = 9.866 T_c$.

The latent heats of fusion per gram-atom of the inactive gases have been calculated.⁴⁷ The value of Eucken's measurement⁴⁸ of the latent heat of fusion of argon, 0.268 kg.cal., is used. The following values were found: helium < 0.004; neon, 0.08; krypton, 0.33; xenon, 0.43; niton, 0.65.

Properties of Liquids; Association.

The constants a and b of van der Waals's equation may be calculated, in the case of normal liquids, from the number of atoms in the molecule, n ; the number of valencies in the molecule, z ; the critical data, and other constants.⁴⁹ The following equations were deduced for the constant b : $b = 412n10^{-6} = 201z10^{-6} = 795.16 \times M^2 10^{-4} / T_s^2 d_s = 12354 d_s 10^{-3} / p_c^2$. The constant a is calculated from the equations: $a = 5.094n T_c 10^{-6} = 2.49z T_c 10^{-6} = 4.5846n^2 p_c 10^{-6} = 1474.713 M^2 10^{-6} / T_s d_s = 23992 d_s T_s 10^{-6} / p_c^2$. The coefficient of expansion of normal liquids may be calculated from a and b .

The "constant" a in Thorpe and Rücker's formula for the dependence of specific volume on temperature: $^{50} V_0/V_t = (aT_c - T)/(aT_c - 273)$ is shown to decrease with increasing temperature.⁵¹ In most series of analogous substances, a increases with the molecular weight; with the exception of the value for water it lies between 1.5 and 2.1.

In the case of organic liquids containing carbon, hydrogen, and oxygen, the relation $n = 193M^2/T_s^2 d_s$ has been deduced by Groshans. If this is combined with the relation $n = 1.1T_c/p_c$ and with Trouton's rule, it follows⁵² that $M/T_s^2 = 0.00077$. This holds with approximate accuracy for compounds ranging from ethane ($T_s = 187.6$) to anthraquinone ($T_s = 653$). By combining Groshans's equation with the relation $v_c = 0.0009n$, it is shown that $v_c = 0.1737M^2/T_s^2 d_s$, or from the above equation, $v_c = 1.34 \times 10^{-4} M/d_s$. The values of

⁴⁶ E. K. Rideal, *Phil. Mag.*, 1921, [vi], **42**, 156; *A.*, ii, 489.

⁴⁷ J. Narbutt, *Physikal. Z.*, 1921, **22**, 52; *A.*, ii, 163.

⁴⁸ Eucken, *Beibl. Ann. Phys.*, 1916, **40**, 322.

⁴⁹ W. Herz, *Z. Elektrochem.*, 1921, **27**, 373; *A.*, ii, 573.

⁵⁰ *T.*, 1884, **45**, 135.

⁵¹ W. Herz, *Z. physikal. Chem.*, 1921, **97**, 376; *A.*, ii, 374.

⁵² W. Herz, *Z. anorg. Chem.*, 1921, **116**, 250; *A.*, ii, 484; compare Jorissen, *A.*, 1920, ii, 90; *A.*, ii, 484; compare also *A.*, 1920, ii, 285.

v_c calculated for a number of esters of fatty acids agree well with those observed. The relation between specific heat s and critical data for the higher paraffins can be expressed by $sM = 2.44T_c/p_c$.

The ratio of molecular volume to density is not constant at corresponding temperatures for normal and associated liquids.⁵³ The ratio d_s/d_c , where d_s and d_c are the densities at the boiling point and at the critical temperature, is 2.69 for monohalogenated benzenes. The assumption of constancy of the ratio of molecular volume to density would give $M_c/M_s = 2.69d_c/d_s$, where M_c and M_s are the molecular weights at the critical temperature and the boiling point. For a number of known associated liquids the ratio was found to be nearly unity. It is concluded that the theory of corresponding states cannot be applied where changes of molecular state occur.

The ratio of the densities of liquid and vapour has been shown to be a function of the reduced temperature T/T_c , and as a first approximation does not depend on the individual properties of the liquid.⁵⁴ The value of B in the equation $B = d_l^2/T \log K$, where d_l = density of liquid and $K = d_l/d_v$ is the ratio just referred to, is found to be practically constant for normal liquids. It shows a slight maximum at the point $T/T_c = 0.60$ to 0.65 and a slight minimum at the point $T/T_c = 0.85$ to 0.90 . In the case of associated liquids, the value of B increases with temperature and exhibits no maximum or minimum.

The equation of Mendeléev: $D_t = D_0(1 - Kt)$, where D_0 and D_t are the densities of a liquid at 0° and t° , and K is a constant, has been tested with benzene, its halogen substitution products, and mixtures of these.⁵⁵ It represents the facts equally for normal and for associated liquids, within the limits of experimental error, and cannot be used to differentiate between the two groups. The constant K for mixtures can probably be calculated by the mixture rule.

Hydrogen has been found to obey the law of rectilinear diameter.⁵⁶ The critical density is calculated as 0.03 at -239.91° .

A relation between the critical data and the chemical constant has been deduced.⁵⁷ The chemical constant is calculated by the equation $C = \lambda_0/4.571T$, where $\lambda = (\lambda_0 + AT - BT^2 - \dots)$

⁵³ W. Herz, *Z. anorg. Chem.*, 1921, **115**, 237; *A.*, ii, 436.

⁵⁴ W. Swientoslawski, *Bull. Soc. chim.*, 1921, [iv], **29**, 499; *A.*, ii, 535; *ibid.*, 507; *A.*, ii, 536.

⁵⁵ W. Herz and J. Meyer, *Z. physikal. Chem.*, 1921, **97**, 381; *A.*, ii, 381.

⁵⁶ E. Mathias, C. A. Crommelin, and H. K. Onnes, *Compt. rend.*, 1921, **172**, 261; *A.*, ii, 256.

⁵⁷ Fr. A. Henglein, *Z. anorg. Chem.*, 1920, **114**, 234; *A.*, ii, 163; *Z. physikal. Chem.*, 1921, **98**, 1.

$(1 - p/p_k)$ is the latent heat and p_k, T_k are the critical constants. Nernst's equation, $C = 0.14\lambda/T_B$, where T_B is the absolute boiling point, follows from van der Waals's equation, $\log p/p_k = a(1 - T_k/T)$. Cederberg's equation, $C = k \log p_k$ (where k is 1.6 in many cases), also follows from this equation, since it is a special case of the more general equation, $C = 1.1 \log p_k/(T_k/T_B - 1)$.

The critical temperature of mercury has been calculated,⁵⁸ from the change of surface tension with temperature, as 1474° . Another calculation⁵⁹ from theoretical considerations gave 1700° , the critical pressure being estimated at 1100 atm.

If in van der Waals's vapour pressure equation the critical temperature is replaced by the expression $\frac{1}{2}(1/K_{20} + 293)$, where K_{20} is the coefficient of expansion at 20° , the value of the constant a is close to, generally greater than, 3 for a number of esters. The critical pressure p_c in the same equation can be replaced by $1/K_{20} + 293/0.88n$, where n is the sum of the valencies of the constituent atoms. The constant in Cederberg's formula (see above) has an abnormally high value for organic compounds, increasing with the molecular weight.⁶⁰

The equation $p = RT(d_1 + d_2)(d_2/d_1)^{(d_1 + d_2)/(d_1 - d_2)}$, where p is the vapour pressure, and d_1 and d_2 are the densities of liquid and vapour, has been deduced.⁶¹ The quantity $d_1 + d_2$ may be regarded as a density factor which is a measure of the cohesive forces per unit mass.

Radiation and the Quantum Theory.

The interpretation of the chemical constant, as given by Nernst and by Sackur, has been criticised.⁶² The chemical constants of zinc (1.62) and cadmium (1.56) have been calculated⁶³ by Nernst's formula. These differ somewhat from the values obtained by Egerton,⁶⁴ from whose results they are deduced, but agree with the value 1.59 given by the Sackur-Stern-Tetrode formula. The theory of the chemical constant, from the point of view of statistical mechanics, has been considered,⁶⁵ and the quantum theory has been applied to the theory of corresponding states.⁶⁶ An expression is

⁵⁸ G. Meyer, *Physikal. Z.*, 1921, **33**, 76; *A.*, ii, 238.

⁵⁹ J. J. van Laar, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 267, 282; *J. Chim. Phys.*, 1920, **18**, 273; *A.*, ii, 83.

⁶⁰ W. Herz, *Z. Elektrochem.*, 1921, **27**, 125; *A.*, ii, 302.

⁶¹ J. H. Shaxby, *Phil. Mag.*, 1921, [vi], **41**, 441; *A.*, ii, 239.

⁶² E. Yamazaki, *J. Tokyo Chem. Soc.*, 1920, **41**, 19; *A.*, ii, 574.

⁶³ G. Heidhausen, *Z. Elektrochem.*, 1921, **27**, 69; *A.*, ii, 240.

⁶⁴ *A.*, 1920, ii, 84.

⁶⁵ W. Schottky, *Physikal. Z.*, 1921, **22**, 1; *A.*, ii, 179.

⁶⁶ A. Byk, *ibid.*, 15; *A.*, ii, 163.

obtained which represents the physical properties of the liquid state, and covers the abnormalities observed with substances of small molecular weight.

In the application of the quantum theory to evaporation,⁶⁷ two formulæ may be used: (1) $L = N\hbar(\nu_2 - \nu_1)$, where ν_1 and ν_2 are the frequencies of the solid or liquid and of the vapour, respectively; (2) $L = \frac{1}{2}N\hbar\{\nu_5 - (\nu_3 + \nu_4)\}$ where ν_3 , ν_4 , and ν_5 are the frequencies of activation of the positive nucleus, of the electron, and the radiation frequency, respectively.

On the basis of the similarity between evaporation and solution, it has been suggested⁶⁸ that Trouton's rule should have an analogue in solution, $\lambda/T = \text{const.}$, where λ is the molecular heat of solution and T the temperature which corresponds, for a state of saturation, with an osmotic pressure of 1 atm. By extrapolation from the results with a number of salts, the value was found to be 30—32. From this the elementary quantity of energy involved when a molecule passes into solution was calculated as $18 \times 10^{-16} \cdot T$ ergs, which is the same as that found for the energy of dissociation of solids and of sublimation.

The applications of statistical methods to chemical equilibria have been reported.⁶⁹ The theory of the velocity of unimolecular reactions from the point of view of the radiation hypothesis has been critically discussed.⁷⁰ It is concluded that the similarity in form between the Arrhenius formula, giving the dependence of reaction velocity on temperature, and Wien's law, for the intensity of radiation as a function of temperature, is purely accidental. The absence of absorption bands where they would be indicated by the hypothesis of activating frequencies, and the fact that the energy available, in the form of radiation, is very much less than required, are urged against the hypothesis. A modification of the radiation hypothesis has been proposed⁷¹ which meets some of the objections. The dependence of the unimolecular reaction constant on temperature can be fairly satisfactorily represented by the expression $k = se^{-Q/RT}$, but the significance of s and Q have been differently interpreted.⁷² It is suggested that Q represents the difference between the energy of the reacting molecules and the average energy of all the molecules of that kind. The

⁶⁷ E. K. Rideal, *Proc. Camb. Phil. Soc.*, 1921, **20**, 291; *A.*, ii, 431.

⁶⁸ R. Audubert, *Compt. rend.*, 1921, **172**, 676; *A.*, ii, 303.

⁶⁹ K. F. Herzfeld, *Physikal. Z.*, 1921, **22**, 186; *A.*, ii, 313.

⁷⁰ I. Langmuir, *J. Amer. Chem. Soc.*, 1920, **42**, 2190; *A.*, ii, 31; compare also M. Polányi, *Z. Physik*, 1920, **3**, 31; *A.*, ii, 179.

⁷¹ R. C. Tolman, *J. Amer. Chem. Soc.*, 1921, **43**, 269; *A.*, ii, 248.

⁷² Compare W. C. McC. Lewis, *T.*, 1918, **113**, 471; Lewis and A. McKeown, *J. Amer. Chem. Soc.*, 1921, **43**, 1288; *A.*, ii, 623.

theoretical conclusions are confirmed by an investigation⁷³ of the photochemical decomposition of nitrogen pentoxide. The frequency corresponding with the critical increment may be calculated from the effect of temperature on the reaction velocity according to the equations: $d \log_e K/dT = E/RT^2$ and $E = Nh\nu$,⁷⁴ but light of this frequency is found not to decompose nitrogen pentoxide. In presence of nitrogen dioxide, however, light of 400–460 $\mu\mu$ accelerates the decomposition of the pentoxide, but this does not take place without the dioxide, or in the dark in presence of dioxide. It is suggested that the nitrogen dioxide acts as a photo-catalyst by absorbing radiation, transforming it through fluorescence and giving it out at a particular frequency which is effective in bringing about the decomposition of the pentoxide. The experimental verification of this hypothesis would certainly lend valuable support to the radiation theory of catalysis.

The quantum theory of chemical reaction leads to the equation $k_1 = \nu e^{-Q/RT}$ for the velocity constant of a unimolecular reaction,⁷⁵ where ν is a frequency and Q the heat of activation. It is assumed that $Q = Nh\nu$, which agrees with the experimental results on the decomposition of phosphine. For bimolecular reactions the equation:

$$k_2 = N\sigma^2\sqrt{8\pi RT}(1/M_A + 1/M_B)e^{-\frac{Q_A + Q_B}{RT}}$$

is deduced, where σ is the mean molecular diameter, M_A and M_B the molecular weights, of A and B , and $Q_A + Q_B$ the total heat of activation. This agrees with experiment. Investigation of the influence of the solvent on the temperature coefficient of reaction velocity has been found,⁷⁶ in the case of similar solvents, in some sense to support the deduction from the radiation hypothesis that there is an inverse proportionality between velocity and temperature coefficient. This does not hold for dissimilar solvents. These are not regarded as simple catalysts, and "the radiation theory does not apply to such cases." Tolman's criticisms of Marcelin's deduction of the equation for reaction velocity (see above) has been examined⁷⁷ and its validity questioned.

Einstein's photochemical equivalence law, $n = Q/h\nu$, where n = no. of molecules decomposed, Q = energy absorbed, ν = fre-

⁷³ F. Daniels and E. H. Johnston, *J. Amer. Chem. Soc.*, 1921, **43**, 53, 72; *A.*, ii, 249. Compare E. C. C. Baly and W. F. Barker, *T.*, 1921, **119**, 662.

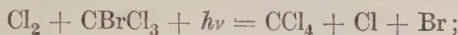
⁷⁴ J. Perrin, *A.*, 1919, ii, 177; W. C. McC. Lewis, *T.*, 1918, **113**, 471.

⁷⁵ S. Dushman, *J. Amer. Chem. Soc.*, 1921, **43**, 397; *A.*, ii, 315.

⁷⁶ H. E. Cox, *T.*, 1921, **119**, 142.

⁷⁷ E. P. Adams, *J. Amer. Chem. Soc.*, 1921, **43**, 1251; *A.*, ii, 628.

quency, has been confirmed ⁷⁸ for the reactions between bromine and *cyclohexane* (gaseous) and chlorine and trichlorobromomethane (liquid). The latter was found to be a good "acceptor" for activated chlorine molecules. A solution of chlorine in the liquid on exposure to light probably undergoes the following reactions:



The bromine could be determined spectrophotometrically; the radiation absorbed was determined by a thermopile as usual. The phenomena are explained on Bohr's theory as follows: a quantum $h\nu$ is absorbed by the chlorine molecule, the valency-electron springs to a larger ring, and the molecule is activated. This active state has a given "life" (calculated as 10^{-10} secs.), during which it may react with an acceptor. If no acceptor is present, the activated molecule gives up energy in the form of other quanta (luminescence, or heat), or transfers it to indifferent molecules, causing a general rise of temperature.

Physical Properties and Chemical Composition.

Some empirical relations between the absolute critical temperature, boiling point, and melting point ⁷⁹ have been shown ⁸⁰ to be purely arithmetical and to have no physical meaning. New relations are deduced from van der Waals's formula $\log p/p_c = f(T_c/T - 1)$, where f may depend slightly on the temperature. If T_1 = boiling point, $p = 1$ atm., then $\phi_1 = T_c/T = \log p_c/f + 1$. ϕ_1 will therefore be approximately constant unless p_c is abnormal (helium). In the case of fusion, $(v_2 - b_2)/v_2 = 1/14$, where $v_2 - b_2$ is the effective volume for molecular motion. Thence $\phi_2 = T_c/T_2 = 2a_c/\gamma a_2$, where T_2 = m. p., a = attraction constant, γ is usually 0.9 but for ideal substances (a and b constant) is 0.5. For ordinary substances, $a_2 = 1.4a_c$; $\phi_2 = 2$. For limiting substances (with T_c from 400° to 500°), $\phi_2 = 1.83$, which agrees with the rule of Timmermans ⁸¹ that the melting points of different families of substances tend to an upper limit of 117° .

The cause of the alternate higher and lower melting points of successive members of the fatty acid series has been explained ⁸²

⁷⁸ W. Noddack, *Z. Elektrochem.*, 1921, **27**, 359; *A.*, ii, 568; see also E. C. C. Baly and W. F. Barker, *T.*, 1921, **119**, 653, for a study of the reaction $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$.

⁷⁹ M. Prud'homme, *J. Chim. phys.*, 1920, **18**, 270, 307, 359; *A.*, ii, 83, 84, 376.

⁸⁰ J. J. van Laar, *J. Chim. phys.*, 1921, **19**, 4; *A.*, ii, 622.

⁸¹ *A.*, ii, 430.

⁸² G. Tammann, *Z. anorg. Chem.*, 1919, **109**, 221; *A.*, 1920, ii, 285.

on the hypothesis that acids with an even number of carbon atoms exist in two stable crystalline forms. In support of this, it was shown that acetic acid exists in two forms with a triple point at 57.5° at 2330 kilos. per sq. cm. No isomerism was found with formic acid. Attention is now ⁸³ directed to the obvious insecurity in basing such a general theory on two observations. It is shown that many other physical properties show the same kind of alternation in homologous series. When the numerical value of the property (solubility, molecular rotation, boiling point) is plotted against the number of carbon atoms, the points corresponding with an even number of carbon atoms lie on one smooth curve, and those corresponding with an odd number on another. These regularities may be explained on the hypothesis ⁸⁴ of the alternate positive and negative character of carbon atoms in a chain. The theory of isomerism, however, is obviously still open to experimental confirmation.⁸⁵

The relation between heats of combustion and constitution has been discussed.⁸⁶ Symmetrical nitro-compounds appear to be most stable.

Guldberg's rule, that the (absolute) boiling point at 1 atm. is equal to two-thirds of the critical temperature, is approximately correct. Atmospheric pressure, however, is not a constant fraction of the critical pressure, and an attempt has been made ⁸⁷ to test the relationship at fractions $\frac{1}{3.3}$ and $\frac{1}{5.0}$ of the critical pressure. With organic liquids $\frac{1}{5.0}$ gave better results, but with inorganic liquids (water, nitrogen, hydrogen sulphide) the constant was lower than with organic liquids.

A linear relation $y = \alpha x + a$ has been found ⁸⁸ to hold between the molecular volume y of one haloid salt and the corresponding volume x of another haloid, the two salts containing a common kation or anion. The question is raised whether the crystalline structure of cæsium haloids is the same as that of the other alkali haloids. The distance between oppositely charged ions in haloid salts is calculated as $r = 0.938 \times 10^{-8} \sqrt[3]{V}$ cm., where V is the molecular volume of the salt.

⁸³ E. J. Cuy, *Z. anorg. Chem.*, 1921, **115**, 273; *A.*, ii, 429.

⁸⁴ *Idem*, *J. Amer. Chem. Soc.*, 1920, **42**, 503; *A.*, 1920, i, 361. Compare A. Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, (iii), 1; *A.*, ii, 543; M. T. Hanke and K. K. Koessler, *J. Amer. Chem. Soc.*, 1918, **40**, 1726; *A.*, 1919, i, 4.

⁸⁵ Compare Tammann, *Z. anorg. Chem.*, 1921, **115**, 288; *A.*, ii, 430.

⁸⁶ O. H. Binder, *Chem. Zeit.*, 1921, **45**, 477; *A.*, ii, 435; W. E. Garner and C. L. Abernethy, *Proc. Roy. Soc.*, 1921, [A], **99**, 213; *A.*, ii, 435; compare *T.*, 1921, **119**, 6.

⁸⁷ R. Lorenz and W. Herz, *Z. anorg. Chem.*, 1921, **115**, 100; *A.*, ii, 433.

⁸⁸ K. Fajans and H. Grimm, *Z. Physik*, 1920, **2**, 299; *A.*, ii, 168.

Theory of Mixtures.

The vapour pressures of liquid mixtures have been considered⁸⁹ from the thermodynamic point of view, and it is shown that the assumption of chemical combination is unnecessary in many cases to explain the results. Evidence of chemical combination was found with sulphuric acid and ethyl ether.

The thermodynamic theory of mixtures,⁹⁰ and the theory of Dolezalek⁹¹ have also been further discussed. An attempt has been made⁹² to apply the latter theory to the electromotive behaviour of alloys.

Electrolytic Conductivity ; Ionisation.

The abnormality of strong electrolytes has been further considered. On the assumption that interionic forces in solution are inverse square functions of the distances apart of dissimilar ions, and that the forces causing dissociation are inverse higher power functions of the distances between molecules, an interpretation of some types of dilution law is obtained.⁹³ Complete ionisation is not assumed, and the law of mass action holds good if active mass is represented by a momentum term. The assumption that the abnormality is due to the abnormal osmotic behaviour of the ions is in entire agreement with the fundamental assumptions made.

The theory of Ghosh⁹⁴ has been further criticised. It is shown⁹⁵ that in his calculation of the number of ions having kinetic energies in excess of a given value ("free ions"), Ghosh has used an incorrect formula. When the correct expression is used, the results are no longer in good agreement with experiment.

The dielectric constants of some electrolytic solutions have been determined.⁹⁶ The electrolytes lowered the dielectric constant of water in a way similar to that of the majority of non-electrolytes.

The limiting value of the molecular conductivity, λ_{∞} , in non-

⁸⁹ A. W. Porter, *Trans. Faraday Soc.*, 1921, **16**, 336; *A.*, ii, 377.

⁹⁰ M. B. Wagner, *Z. physikal. Chem.*, 1920, **96**, 287; 1921, **97**, 229, 330, 337, 343; *A.*, ii, 162, 300, 375; compare *A.*, 1920, ii, 596, 597.

⁹¹ *A.*, 1909, ii, 22; 1913, ii, 482; H. Cassel, *Z. Physik*, 1920, **2**, 146; *A.*, ii, 166; A. Schulze, *Z. physikal. Chem.*, 1921, **97**, 388, 417; *A.*, ii, 388, 390.

⁹² F. Clotofski, *Z. anorg. Chem.*, 1920, **114**, 1; *A.*, ii, 203.

⁹³ W. Hughes, *Phil. Mag.*, 1921, [vi], **42**, 134, 428; *A.*, ii, 481, 573.

⁹⁴ *T.*, 1918, **113**, 449, 627, 707, 790; compare *Ann. Reports* for 1918 and 1919.

⁹⁵ D. L. Chapman and H. J. George, *Phil. Mag.*, 1921, [vi], **41**, 799; *A.*, ii, 371; compare H. Kallmann, *Z. physikal. Chem.*, 1921, **98**, 433.

⁹⁶ R. T. Lattey, *Phil. Mag.*, 1921, [vi], **41**, 829; *A.*, ii, 426.

aqueous and aqueous solutions has been discussed.⁹⁷ According to the Ostwald-Bredig rule, the value of λ_∞ is related to λ_v , at the dilution v , by the formula $\lambda_\infty = \lambda_v + d_v$, where d_v is a constant depending only on the dilution. If the value of λ_∞ is calculated by the formula $\lambda_\infty = \lambda_v + b'/v^{0.45}$,⁹⁸ the values of d_v can be calculated for each solvent for different dilutions. It was found that the Ostwald-Bredig rule can be applied to water and fifteen organic solvents through the range of dilutions $v = 256$ to $50,000$. From general considerations, it was deduced that the product $d_v \cdot \epsilon \cdot \eta_\infty$ should be constant at a particular dilution for all solvents, ϵ being the dielectric constant and η_∞ the viscosity. This was confirmed, and it was further found that by introducing the dilution factor $v^{0.45}$ an expression is obtained which is general for all solvents (including water) and solutes at all dilutions: $d_v \cdot \epsilon \cdot \eta_\infty \cdot v^{0.45} = \text{const.} = 51.4$. Thus, if ϵ and η_∞ are known for the solvent, d_v can be calculated for any dilution. Thence, from a single observation of λ_v , the value of λ_∞ , and from it $\alpha = \lambda_v/\lambda_\infty$, can be found. It is shown⁹⁹ that the product $\lambda_\infty \eta_\infty$ is constant for all ionising solvents; it is independent of the temperature between 0° and 25° , but depends, within limits, on the nature of the solute. The above general expression may be written $(1 - \alpha)\epsilon \cdot v^{0.45} = 51.4/\lambda_\infty \eta_\infty = \text{const.}$, which shows that, if $\lambda_\infty \eta_\infty$ is known for a salt in any one solvent, its degree of ionisation in any other solvent at any dilution may be calculated. The diameters of ions in aqueous solutions have been calculated¹ from Einstein's diffusion formula: $U = K/N \cdot 6\pi\eta\rho$, where U = velocity, ρ = radius, of particle, K = force acting on particle, N = Avogadro's number, η = viscosity. For most ions, ρ lies between 2.0×10^{-8} cm. and 3.9×10^{-8} cm., but is abnormal for hydrogen (1.1×10^{-8}) and lithium (4.7×10^{-8}). The ionic radii in non-aqueous follow the same order as in aqueous solutions: $\text{H}^+ < \text{K}^+ < \text{Ag}^+ < \text{Na}^+ < \text{Li}^+$; $\text{Br}^- < \text{I}^- < \text{Cl}^- < \text{NO}_3^-$, but in the former the values are about twice as great (mean values 2.67 and 5.33×10^{-8} cm.). Organic anions and kations have the same radius in both solutions (4.4×10^{-8}). Much greater solvation in non-aqueous solutions is assumed.

The sizes of the ions in crystal lattices, calculated by a modification of Born's theory, were found to be,² in 10^{-8} cm.:—Na 0.517; K 0.794; Rb 0.914; F 0.75; Cl 0.953; Br 1.021; I 1.122. The energies of the alkali haloid lattices, in kg. cal., were calculated:

⁹⁷ P. Walden, *Z. anorg. Chem.*, 1920, **113**, 113; *A.*, ii, 170; *ibid.*, 1921, **115**, 49; *A.*, ii, 423.

⁹⁸ R. Lorenz, *A.*, 1920, ii, 6.

⁹⁹ P. Walden, *Z. anorg. Chem.*, 1920, **113**, 85; *A.*, ii, 160.

¹ P. Walden, *ibid.*, 125; *A.*, ii, 171.

² K. Fajans and K. F. Herzfeld, *Z. Physik*, 1920, **2**, 309; *A.*, ii, 174.

NaF 210.4; NaCl 170.0; NaBr 159.7; NaI 146.7; RbBr 146.5; RbI 135.8.

The theory of Hertz has been further developed.³ The value of Hertz's "constant," A , is not 18.9, but is different for each ion. The radii of a number of ions are calculated.

The electrolytic conductivities of a number of molten salts, at temperatures to 1600° have been determined.⁴

The radius of an ion may be calculated⁵ from the formula $W = \frac{1}{2}(1 - 1/\epsilon)N \cdot 2388 \times 10^{-11}e^2z^2/r_i$ Cal., where W = heat of hydration,⁶ N = Avogadro's constant, z = valency, e = charge on electron, r_i = radius of ion, ϵ = dielectric constant of solvent. The values of r_i and of r_a (the atomic radius) are calculated, and it is shown that (except in the case of thallium) for positive ions $r_i < r_a$, whilst for negative ions $r_i > r_a$. This is explained by the increase in volume in the formation of negative ions by the absorption of an electron into the atomic structure, and the decrease in volume when a positive ion is formed by removal of an electron from the atom.

The dissociation of ternary electrolytes has been investigated⁷ in the cases of sulphuric, oxalic, and tartaric acids, and the normal and hydrogen salts of these acids with thallium and potassium. Solutions of concentrations below 0.04*N* follow the law of mass action, and in certain cases this holds at even higher concentrations.

The ionisation of tetramethylammonium thiocyanate (a strong electrolyte) is practically the same ($\alpha = 0.38$) in saturated solutions in nine non-aqueous solvents.⁸ The solubility of the same salt in different non-aqueous solvents is, approximately, given by $\epsilon/\mu^{\frac{1}{3}} = 34$, where ϵ = dielectric constant, μ = molecular solubility.

The "objection" to the electrolytic dissociation theory due to Kahlenberg, and quoted in most text-books, is shown⁹ to rest on inaccurate experiments. Benzene solutions of salts of organic acids (copper oleate, barium crucate, copper stearate, and silver melissate),

³ R. Lorenz, *Z. anorg. Chem.*, 1920, **113**, 131; *A.*, ii, 158; *ibid.*, 135; *A.*, ii, 158; R. Lorenz and P. Osswald, *ibid.*, 114, 209; *A.*, ii, 158; R. Lorenz and W. Neu, *ibid.*, 1921, **116**, 45; *A.*, ii, 481; R. Lorenz and W. Michael, *ibid.*, 161; *A.*, ii, 482; R. Lorenz and A. Scheuermann, *ibid.*, 121, 140; *A.*, ii, 482, 483; compare *Ann. Reports*, 1920.

⁴ F. M. Jaeger and B. Kapma, *ibid.*, 1920, **113**, 27; *A.*, ii, 160.

⁵ M. Born, *Z. Physik*, 1920, **1**, 45; *A.*, ii, 166.

⁶ See *Ann. Reports*, 1920; A. von Weinberg, *Z. Physik*, 1920, **3**, 337; *A.*, ii, 165; A. Reis, *ibid.*, 1920, **1**, 294; *A.*, ii, 166.

⁷ C. Drucker, *Z. physikal. Chem.*, 1920, **96**, 381; *A.*, ii, 161.

⁸ P. Walden, *Z. Elektrochem.*, 1921, **27**, 34; *A.*, ii, 309.

⁹ H. P. Cady and E. J. Baldwin, *J. Amer. Chem. Soc.*, 1921, **43**, 646; *A.*, ii, 309.

which give precipitates with dry hydrogen chloride, showed a conductivity before and during reaction.

Evidence of the ionisation of gases during chemical change has been obtained,¹⁰ in the cases: $\text{Cl}_2 + 2\text{NO} = 2\text{NOCl}$; $2\text{O}_3 = 3\text{O}_2$; and the reaction between ozone and nitric oxide or nitrogen dioxide.

Electromotive Forces.

The use of a saturated KCl-calomel electrode has been proposed¹¹ for use in *E.M.F.* measurements in place of 0.1*N*- and *N*-calomel electrodes. On the assumption that the absolute potential of the *N*-calomel electrode at 25° is 0.5648 volt, that of the saturated potassium chloride electrode is 0.5266 volt, with a temperature coefficient of + 0.00020 volt/degree from 5° to 60°. A saturated salt bridge is used.

The hydron concentration in pure water has been found¹² to be 1.23×10^{-8} by a method depending on charging a condenser first with the cell $\text{Hg}|\text{HgCl}, \text{KCl}|\text{KCl}|\text{H}_2\text{O}|\text{H}_2$, and then with a standard cell, and in each case discharging through a galvanometer.

Further measurements of the heat of formation of silver iodide by *E.M.F.* methods have been made.¹³ The discrepancy between the results of Fischer¹⁴ and of Jones and Hartmann¹⁵ has been shown to depend on the uncertainty in the correction for I_3' ions in the potassium iodide solution, this being now determined experimentally, and on the use of electrochemically purer silver electrodes by Fischer. The value 15,158 cal. is obtained, which, compared with Fischer's value of 15,169 cal. and that of Jones and Hartmann (14,570), points to the greater accuracy of the former value.

The effect of fluorescent dyes on the *E.M.F.* of illuminated cells has been studied,¹⁶ both alone and in presence of oxidising and reducing substances. The Becquerel effect was observed, and the behaviour of the cells can be explained on the hypothesis of a concealed oxygen-hydrogen photolysis. This has been confirmed¹⁷ by using a fluorescent substance in an electrolytic cell, when a depolarising action was clearly noticed.

The thermodynamic treatment of concentrated solutions, with

¹⁰ A. Pinkus and M. de Schulthess, *J. Chim. phys.*, 1920, **18**, 366; *Helv. Chim. Acta*, 1921, **4**, 288; *A.*, ii, 368; compare O. W. Richardson, *Phil. Trans.*, 1921, [A], **222**, 1; *A.*, ii, 422.

¹¹ H. A. Fales and W. A. Mudge, *J. Amer. Chem. Soc.*, 1920, **42**, 2434; *A.*, ii, 79.

¹² H. T. Beans and E. T. Oakes, *ibid.*, 2116; *A.*, ii, 12.

¹³ O. Gerth, *Z. Elektrochem.*, 1921, **27**, 287; *A.*, ii, 534.

¹⁴ *A.*, 1912, ii, 536, 1054.

¹⁵ *Ibid.*, 1915, ii, 308.

¹⁶ E. Staechelin, *Z. physikal. Chem.*, 1920, **94**, 542; *A.*, 1920, ii, 580.

¹⁷ E. Baur, *Z. Elektrochem.*, 1921, **27**, 72; *A.*, ii, 236.

special reference to the *E.M.F.*'s of amalgams, has been developed.¹⁸ The electromotive properties of a number of binary alloys have been studied.¹⁹ With thallium and thallium-lead alloys, the potentials with 0 to 20 atom. per cent. of lead are practically equal to those of thallium; from 50 to 100 atom. per cent. of lead they are equal to the lead potentials; between 20 and 50 atom. per cent. of lead the potentials pass into one another asymptotically.

Experiments on thermo-elements²⁰ showed that copper-phosphorus alloys did not give a favourable ratio of thermal to electrical conductivity, which is inversely proportional to the efficiency of a thermo-couple. Antimony-cadmium alloys with approximately atomic composition show probably the highest thermoelectric power of all metals and alloys hitherto investigated. The influence of heat treatment is of importance in investigating the effect of temperature on *E.M.F.* Amalgamation depresses thermoelectric power. The effect of pressure on a solid junction of two materials has been calculated²¹ on the assumption of material transport with the current. The measurement of the resulting "bary-electromotive force" would give the transport numbers in solid electrolytes and the ratio of electronic to material conduction in poor conductors.

Chemical Dynamics and Equilibrium.

An investigation²² of the catalytic decomposition of hydrogen peroxide by sodium iodide in aqueous mixtures of alcohols, glycerol, and pyridine failed to disclose any relation between the velocity of reaction and the dielectric constant, viscosity, or surface tension of the pure solvent; the latter appears to exert a specific influence. The effect of mercuric ions on the velocity of oxidation of arsenious acid by nitric acid is peculiar.²³ At a concentration of 7.7×10^{-6} mol. per litre the reaction was completely inhibited. With diminishing concentration, the inhibiting effect of the mercuric ions became less marked down to a concentration of 7.7×10^{-8} ,

¹⁸ G. N. Lewis and M. Randall, *J. Amer. Chem. Soc.*, 1921, **43**, 233; *A.*, ii, 241.

¹⁹ R. Kremann, *Z. Metallkunde*, 1920, **12**, 185; *Chem. Zentr.*, 1920, iii, 684; *A.*, ii, 10; R. Kremann and H. Ruderer, *ibid.*, 1920, **12**, 209; *Chem. Zentr.*, 1920, iii, 684; *A.*, ii, 11; R. Kremann and J. Gmachl-Pammer, *Int. Z. Metal.*, 1920, **12**, 241; *Chem. Zentr.*, 1921, i, 123; *A.*, ii, 156.

²⁰ G. Pfeleiderer, *Ges. Abhandl. Kennt. Kohle*, 1919, **4**, 409; *Chem. Zentr.*, 1921, i, 348; *A.*, ii, 296; F. Fischer and G. Pfeleiderer, *ibid.*, 440; *Chem. Zentr.*, 1921, i, 349; *A.*, ii, 296.

²¹ M. Polányi, *Z. physikal. Chem.*, 1921, **97**, 459; *A.*, ii, 372.

²² Van L. Bohnson, *J. Physical Chem.*, 1920, **24**, 677; *A.*, ii, 185.

²³ A. Klemenc and F. Pollak, *Z. anorg. Chem.*, 1921, **115**, 131; *A.*, ii, 442.

and at 7.7×10^{-9} there was a positive catalytic effect, which became still more marked at 7.7×10^{-11} mol. per litre. The smallest measured effective concentration of catalyst previously recorded is 7×10^{-6} for colloidal platinum in the decomposition of hydrogen peroxide.

The kinetics of the reduction of azo-compounds by acid stannous chloride has been studied.²⁴ The reaction is bimolecular, and in cases where the azo-compound is broken up into two amino-derivatives it occurs in two stages. The reduction to hydrazo-compound takes place first with measurable velocity; further reduction then occurs with extreme rapidity.

The kinetics of the formation of acetone from acetoacetic acid in acid and in alkaline solution has been studied.²⁵ In the second case, practically only the anion $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2'$, whilst in strongly acid solution practically only undissociated acetoacetic acid, is present. The undissociated and dissociated acids show very different velocities of decomposition; that of the former is fifty times the greater. In almost neutral solutions, the rate of decomposition depends on the ionisation of the acid.

Many reactions having large temperature coefficients are sensitive to light,²⁶ hence it is concluded that sensitiveness to temperature and to light influences have a common cause, in agreement with Perrin's radiation hypothesis.²⁷

A number of abnormally large and small temperature coefficients have been explained²⁸ by hydrolysis of some salt present. The reaction between iodic acid and potassium iodide in dilute solutions is very rapid at 0° . In presence of sodium and magnesium sulphates, slightly less iodine is liberated at higher than at lower temperatures. This apparent negative coefficient is due to hydrolysis of the sulphate at higher temperatures, with formation of OH' ions. The abnormally large temperature coefficient of the reaction $3\text{I}_2 + 6\text{OH}' = 5\text{I}' + \text{IO}_3' + 3\text{H}_2\text{O}$ in presence of sodium carbonate and sodium hydrogen carbonate is due to hydrolysis of these salts.

A study²⁹ of induced reactions led to the hypothesis that the substance in which oxidation is induced (sodium arsenite) acts as a negative catalyst towards the substance which induces the

²⁴ H. Goldschmidt and A. Braanaas, *Z. physikal. Chem.*, 1920, **96**, 180; *A.*, ii, 184.

²⁵ E. M. P. Widmark, *Acta Med. Scandinav.*, 1920, **53**, 393; *Chem. Zentr.*, 1921, i, 9; *A.*, ii, 183.

²⁶ N. R. Dhar, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 308; *A.*, ii, 37.

²⁷ *A.*, 1919, ii, 177.

²⁸ N. R. Dhar, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 313; *A.*, ii, 37.

²⁹ *Idem, ibid.*, 1921, **23**, 1074; *A.*, ii, 391.

oxidation (sodium sulphite). The formation of a complex of the two oxidisable substances, the less oxidisable constituent of which is more easily oxidised, is assumed.

In a study of the keto-enolic tautomerism of benzoylcamphor,³⁰ it was found that the results obtained by K. H. Meyer's method³¹ of titration with bromine do not agree with the equation $c_A/c_B = Kl_A/l_B$, where c_A , c_B are the equilibrium concentrations, l_A , l_B the solubilities, and K is a constant independent of the nature of the solvent.³² When the method of optical activity³³ was used, a satisfactory agreement was found, and the ratios of the enol/ketone forms in equilibrium in different solvents were found to be: in toluene, 82/18; in alcohol, 61/39; in acetone, 52/48. At -83° , both forms should co-exist in the crystalline state.

A new method for the determination of the vapour pressure of salt hydrates is described.³⁴ It consists in the establishment of equilibrium between the hydrates and a solution of water in *iso*-amyl alcohol, followed by an estimation of the water content of the resulting liquid. (With salts of small vapour pressure, a simple method would appear to be a determination of the freezing point of benzene in equilibrium with the salt.)

Variations with time in the activity of colloidal platinum have been studied.³⁵ The catalytic power is attributed to a metal-oxygen complex, and the initial rise of activity to increase of oxygen concentration. The oxide theory is also supported by other workers.³⁶

The conditions which control the accuracy of titration of mixtures of acids and bases, from the point of view of suitable choice of indicator, have been described.³⁷

The increase in size of particles of a precipitate in contact with a liquid is usually ascribed to the (experimentally verified) difference in solubility of large and small crystals. It has been suggested³⁸ that it is due to "irreversible transformation of secondary aggre-

³⁰ H. Vixebøse, *Rec. trav. chim.*, 1921, **40**, 1; *A.*, ii, 179.

³¹ *A.*, 1911, i, 350, 832.

³² Van't Hoff, quoted by Dimroth, *A.*, 1911, ii, 31; 1913, ii, 763; compare Smits, *A.*, 1915, ii, 750.

³³ M. O. Forster, *T.*, 1901, **79**, 987.

³⁴ R. E. Wilson, *J. Amer. Chem. Soc.*, 1921, **43**, 704; *A.*, ii, 376; A. A. Noyes and L. R. Westbrook, *ibid.*, 726; *A.*, ii, 377.

³⁵ A. de G. Rocasolano, *Compt. rend.*, 1921, **173**, 41, 234; *Anal. Fis. Quím.*, 1920, **18**, 308, 361; 1921, **19**, 114; *A.*, 1920, ii, 479, 607; 1921, ii, 251, 321, 390, 498, 542.

³⁶ R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, 1921, **54**, [B], 113; *A.*, ii, 185.

³⁷ H. T. Tizard and A. R. Boeree, *T.*, 1921, **119**, 132.

³⁸ S. Odén, *Svensk. Kem. Tidskr.*, 1920, **32**, 108; *A.*, ii, 25.

gates primarily formed." Reversibility appears to depend on the degree of hydration of the particles which are attached to one another by aqueous envelopes. If these are broken, or if the original hydration is too slight (for example, with metallic particles) the transformation becomes irreversible.

The effect of one solute, A , in lowering the solubility of a second solute, B , in a given solvent has been shown to be represented³⁹ by the simple equation $\log(s_0/s) = kc$, where s_0 , s are the solubilities of B in the pure solvent and in a solution of A in B of concentration c , and k is a constant.

Heterogeneous Reactions.

The influence of physical conditions on the velocity of decomposition of some crystalline solids was investigated⁴⁰ in the cases of the evolution of gas by heat from silver permanganate, potassium permanganate, ammonium dichromate, and solid solutions of potassium permanganate and potassium chlorate. The conclusion is drawn that the rate of decomposition is largely dependent on the surface of the solid, that the effective surface is considerably greater than the apparent surface, and that solid crystals may be assumed to be aggregates loosely held together. The results with solid solutions support the hypothesis that the process of solid mixture leads to increased chemical stability, from the heat of mixture.

The reduction of cotton-seed oil by hydrogen in presence of metallic nickel at 180° ⁴¹ shows that the variations in catalytic power of reduced nickel may be referred to the different surfaces of nickel exposed. In the catalytic reduction of ethylene to ethane in presence of nickel, an induction period was noticed,⁴² followed by a sharp maximum velocity. It is supposed that hydrogen is selectively adsorbed, whilst ethylene is adsorbed only after activation (chiefly by "thermal contact" with a molecule undergoing hydrogenation). The nickel at first becomes covered with hydrogen molecules. Reaction of these with ethylene molecules occurs, the heat liberated being communicated to the surrounding molecules. Hydrogen is then volatilised and activated ethylene deposited.

The relation between the occlusive power of palladium for hydrogen and its catalytic activity has been studied,⁴³ lead being

³⁹ P. C. L. Thorne, *T.*, 1921, **119**, 262; compare W. Nernst, *Z. physikal. Chem.*, 1890, **6**, 16.

⁴⁰ C. N. Hinshelwood and E. J. Bowen, *Proc. Roy. Soc.*, 1921, [*A*], **99**, 203; *A.*, ii, 443; compare *Phil. Mag.*, 1920, [vi], **40**, 569; *A.*, 1920, ii, 743.

⁴¹ E. F. Armstrong and T. P. Hilditch, *ibid.*, 490; *A.*, 1920, ii, 582.

⁴² D. M. and W. G. Palmer, *ibid.*, 402; *A.*, ii, 541.

⁴³ E. B. Maxted, *T.*, 1921, **119**, 1280.

the inhibitant. The relation is linear from the point corresponding with zero concentration of the poison up to a stage where the greater part of the activity has been suppressed. In this region a point of inflexion occurs, beyond which the rate of decrease in catalytic activity due to further addition of lead falls off much less rapidly than on the main part of the curve. The amount of lead required to reduce the catalytic activity to half is very much less than that which reduces the occlusive power to half its original value. This may be explained by the fact that, whilst the occlusion is not confined to the surface, catalysis is mainly a surface phenomenon. Measurements of the adsorption of gases by metallic catalysts⁴⁴ show that it is a specific property of the metal, depending on the mode of preparation, being less the higher the temperature to which the metal has been subjected. Destruction of catalytic activity is accompanied by almost complete suppression of adsorptive power. Maximum catalytic activity does not occur at temperatures at which maximum adsorption is shown. A strong or irreversible adsorption of any one of the reacting substances tends to render the catalyst inactive. Reaction is the resultant of two factors, adsorption and temperature. The adsorptive capacity is an index of the temperature at which reaction can be induced. Where adsorption is strong, a lower temperature may effect interaction.

Combustion and Explosion Reactions.

The mechanism of reaction in some cases of combustion has been studied⁴⁵ and the conclusion is drawn that reaction is preceded by the formation of an unstable additive compound. The minimum amount of moisture necessary to promote explosion of carbon monoxide with oxygen or nitrous oxide corresponds with a partial pressure of 0.5 mm. The reaction is formulated as follows : (1) $\text{CO} + \text{H}_2\text{O} = \text{H}\cdot\text{CO}_2\text{H}$; (2) $\text{H}\cdot\text{CO}_2\text{H} = \text{CO}_2 + \text{H}_2$; (3) $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$; (4) $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$. The presence of hydrogen in the carbon monoxide flame was proved by its passage through palladium. Hydrogen peroxide was detected when the gas was passed through a heated quartz tube, cooled in the further part. An indication of a peroxide-like substance was also obtained in the combustion of cyanogen.

The influence of carbon dioxide on the pressure limit of phosphorescence of phosphorus in oxygen and on the inferior limits of explosion of hydrogen and methane is greater than that of

⁴⁴ H. S. Taylor and R. M. Burns, *J. Amer. Chem. Soc.*, 1921, **43**, 1273; *A.*, ii, 630.

⁴⁵ H. von Wartenberg and B. Sieg, *Ber.*, 1920, **53**, [B], 2192; *A.*, ii, 107.

nitrogen.⁴⁶ The point of inflammation of various mixtures of hydrogen and oxygen, defined as the temperature at which the reaction velocity exceeds a measurable value, has been measured⁴⁷ by bringing both gases to the required temperature and determining by a membrane manometer whether rapid reaction occurs on mixing. The minimum inflammation point, 397.5° , was found with $3\text{H}_2 + 2\text{O}_2$; for $\text{H}_2 + \text{O}_2$ it is 407° , and increases after the minimum to 433° for $4\text{H}_2 + \text{O}_2$ (in all cases for dry gases). With moist gases, the results were rather irregular. The reaction between moist oxygen and hydrogen is bimolecular; with absolutely dry gases, it would seem to be termolecular. The possibility of velocity measurements is discussed.

A detailed study of the propagation of combustion in gaseous mixtures from the point of view of Hugoniot's law has appeared.⁴⁸ The phenomenon of successive explosions has also been investigated.⁴⁹ Measurements of the heat loss by conduction and radiation during the explosion and subsequent cooling of mixtures of coal gas and air indicate⁵⁰ that at the moment of maximum pressure about 10 per cent. of the heat of combustion has not been converted into thermal energy and that after-burning continues for at least 0.25 sec. after the attainment of the maximum pressure.

Reference may be made to the important monograph on the properties of explosives contributed in a special lecture to the Society.⁵¹

A piezoelectric method of measuring explosion pressures has been described.⁵²

The modes of ignition of mixtures of hydrogen and of carbon monoxide with oxygen have been studied⁵³ by measurements of the rate of rise of pressure. In the second case, there is a slower rise of pressure and evolution of heat for a relatively long time after the attainment of the maximum pressure.

Colloids.

Determinations of the radii of ultramicroscopic gold and silver particles (a) from the colour, (b) from the Brownian movement,

⁴⁶ W. P. Jorissen, *Rec. trav. chim.*, 1920, **39**, 715; *A.*, ii, 99; compare *A.*, 1919, ii, 62.

⁴⁷ H. Fiesel, *Z. physikal. Chem.*, 1921, **97**, 158; *A.*, ii, 317.

⁴⁸ L. Crussard, *Technique moderne*, 1920, **12**, 243, 295; *A.*, ii, 32.

⁴⁹ A. Stavenhagen and F. Schuchard, *Z. angew. Chem.*, 1920, **33**, 286; *A.*, ii, 33.

⁵⁰ W. T. David, *Proc. Roy. Soc.*, 1921, **98**, [A], 303; *A.*, ii, 85.

⁵¹ (Sir) R. Robertson, *T.*, 1921, **119**, 1.

⁵² D. A. Keys, *Phil. Mag.*, 1921, [vi], **42**, 473; *A.*, ii, 628.

⁵³ W. A. Bone and W. A. Haward, *Proc. Roy. Soc.*, 1921, [A], **100**, 67; *A.*, ii, 628.

showed no systematic variation between the two series.⁵⁴ The degree of dispersity of sols with particles so small as to be invisible in the ultramicroscope may, as is known,⁵⁵ be found by allowing the particles to act as nuclei for the deposition of gold. This method of "gilding" has been⁵⁶ applied to determine the radius of amicrons. Smoluchowski's formula⁵⁷ for the velocity of flocculation is verified⁵⁸ for the rapid, but not for the slow, flocculation of a selenium sol. The limiting size of a particle which exhibits Brownian movement has been found⁵⁹ to be 2.6μ for a number of metals. In different liquids, the logarithm of the limiting size was found to give a straight line when plotted against the viscosity: $a\eta^{0.229} = 3.5$ for gold; $a\eta^{0.249} = 3.4$ for copper.

A series of investigations on soap curds⁶⁰ has confirmed and extended the ultramicroscopic investigations of Zsigmondy and Bachmann.⁶¹ It is shown that soap may exist in three distinct hydrated forms: sol and gel (transparent) and curd (opaque).

The physical-chemical analysis of ferric hydroxide sols shows⁶² that this substance is a complex salt of the type $x\text{Fe}(\text{OH})_3y\text{Fe}/\text{An}$, where An is the anion in presence of which the sol is formed.

The modulus of rigidity of gelatin gels at different concentrations, under torsion, follows Hooke's law nearly up to the breaking point.⁶³ The modulus of elasticity, E , and the concentration, c , are related by $E = kc^n$ over a limited range, but the constants k and n differ for different grades of gelatin. The elasticity is not a simple function of the hydrogen-ion concentration. Gelatin gels may represent any transition stage between a two-phase structure and a physically homogeneous system in which mechanical strength must be attributed to solution forces.

Three-phase emulsions may be obtained⁶⁴ by shaking pairs of immiscible liquids, such as water and benzene, with alumina, zinc

⁵⁴ R. Fürth, *Physikal. Z.*, 1921, **33**, 80; *A.*, ii, 243.

⁵⁵ Zsigmondy, *A.*, 1906, ii, 679.

⁵⁶ G. Börjeson, *Kolloid Z.*, 1920, **27**, 18; *A.*, ii, 27.

⁵⁷ *A.*, 1917, ii, 297.

⁵⁸ H. R. Kruyt and A. E. van Arkel, *Rec. trav. chim.*, 1920, **39**, 656; *A.*, ii, 25 (compare *A.*, 1919, ii, 140; 1920, ii, 739); *ibid.*, 169; *A.*, ii, 312.

⁵⁹ B. Arakatsu and M. Fukuda, *Mem. Coll. Sci. Kyoto*, 1920, **4**, 179; *A.*, ii, 175.

⁶⁰ J. W. McBain, W. F. Darke, and C. S. Salmon, *Proc. Roy. Soc.*, 1921, [*A*], **98**, 395; *A.*, ii, 312; McBain and M. E. Laing, *T.*, 1920, **117**, 1506; McBain and H. E. Martin, *ibid.*, 1921, **117**, 1369; McBain and Salmon, *ibid.*, 1374.

⁶¹ *A.*, 1913, ii, 194.

⁶² W. Pauli, *Kolloid Z.*, 1921, **28**, 49; *A.*, ii, 246.

⁶³ S. E. Sheppard and S. S. Sweet, *J. Amer. Chem. Soc.*, 1921, **43**, 539; *A.*, ii, 311.

⁶⁴ H. Bechold, L. Dede, and L. Reiner, *Kolloid Z.*, 1921, **28**, 6; *A.*, ii, 177.

dust, or yeast, and an "emulsion promoter," such as pyridine, acetic acid, ethyl alcohol, or sodium nitrate. The relative surface tensions of the two liquids have no influence on the emulsification.

The influence of the concentration of a sol on the coagulative power of any given ion has been investigated.⁶⁵ For univalent ions, the concentration to produce coagulation increases with decreasing concentration of the colloid, very rapidly at low values of the latter. For bivalent ions, the ion concentration is almost constant, and thus independent of the concentration of the colloid. For trivalent ions, the coagulating concentration is almost proportional to the colloid concentration. At least two properties of the system colloid + electrolyte seem to be involved. The influence of dilution and quantity of electrolyte on flocculation has also been considered.⁶⁶ The velocity of flocculation, with a constant quantity of electrolyte and colloid, at first diminishes as the dilution of electrolyte increases, but tends to a limit when the dilution reaches a certain value. When the amount of electrolyte is varied but the concentration kept constant, the velocity of flocculation increases with the amount of electrolyte used.

In a study⁶⁷ of the swelling of gelatin, it is concluded that the swelling is the result of osmotic pressure within the gel, the latter acting as an imperfectly resisting membrane.

Investigations on proteins⁶⁸ show that the Hofmeister series is not the correct expression of the relative effects of ions on the swelling of gelatin. The valency, not the nature, of the ion in combination with gelatin affects the degree of swelling. Results depend on the effect of the salt added on the hydrogen-ion concentration of the protein solution.

The electro-endosmose of a number of solutions with various membranes has been investigated.⁶⁹ The charge on which the electro-endosmosis depends can be attributed to ionic adsorption.

The precipitation of colloids by electrolytes has been considered⁷⁰ from the point of view of the surface forces exerted by heteropolar crystal lattices on adsorbed ions. The results were confirmed by measurements of the adsorption of thorium-*B* by silver haloids. Those ions are strongly adsorbed by an ionic space lattice which

⁶⁵ E. F. Burton and E. Bishop, *J. Physical Chem.*, 1920, **24**, 701; *A.*, ii, 176.

⁶⁶ A. Boutaric and M. Vuillaume, *Compt. rend.*, 1921, **173**, 229; *A.*, ii, 537.

⁶⁷ C. R. Smith, *J. Amer. Chem. Soc.*, 1921, **43**, 1350; *A.*, i, 749.

⁶⁸ J. Loeb, *J. Gen. Physiol.*, 1920, **3**, 247; *A.*, i, 136; *ibid.*, 1921, **3**, 391; *A.*, i, 367; compare *A.*, 1920, i, 894.

⁶⁹ A. Gyemant, *Kolloid Z.*, 1921, **28**, 103; *A.*, ii, 298.

⁷⁰ K. Fajans and K. von Beckerath, *Z. physikal. Chem.*, 1921, **97**, 478; *A.*, ii, 386.

forms sparingly soluble compounds with the oppositely charged constituent of the lattice.

It has been shown that arsenic trisulphide sols are photochemically active.⁷¹ Colloidal sulphur is formed by exposure to light.

The precipitation of arsenious sulphide sols by cobaltammine ions has been applied⁷² to determine the valency of the ions. The limiting concentration of the precipitating solution can be expressed by the formula $S_N = S_1/N^4$, where S_N is the equivalent concentration of an N -valent ion and S_1 the limiting concentration for a univalent ion. This is deduced theoretically from the adsorption formula.

A comparison of the protective effect, and the inhibiting influence on catalytic decomposition, of colloids,⁷³ has shown that the two are parallel. Soaps are regarded as colloidal even at great dilution.

Adsorption.

Freundlich's rule, that the order in which substances are adsorbed is almost independent of the nature of the solid phase, has been confirmed⁷⁴ with various kinds of charcoal. Except in the case of iodine, the adsorption isotherm, $x/m = \alpha c^{1/n}$ was found to hold, the constant α being taken as an index of the adsorptive power. The adsorption of iodine by carbon in different forms, in benzene and chloroform, has been studied⁷⁵ over periods of time extending to five years. A rapid condensation of iodine takes place in the first few minutes, followed by a much slower "sorption" continuing for months or years. The first condensation is attributed to true adsorption, the second to slow absorption.

The adsorption of salts by silver powder⁷⁶ lends support to Polányi's theory⁷⁷ that the adsorbed ions form several molecular layers.

The adsorption equilibrium between fatty acids in aqueous solution and charcoal is displaced⁷⁸ by neutral salts in the sense that more acid is adsorbed. The amounts of cation and anion adsorbed by carefully purified charcoal from aqueous solutions of

⁷¹ H. Freundlich and A. Nathansohn, *Kolloid Z.*, 1920, **28**, 258; *A.*, ii, 494.

⁷² K. Matsuno, *J. Coll. Sci. Tokyo*, 1921, **41**, ii, 1; *A.*, ii, 637.

⁷³ T. Iredale, *T.*, 1921, **119**, 109, 625.

⁷⁴ I. M. Kolthoff, *Pharm. Weekblad*, 1921, **58**, 630; *A.*, ii, 383.

⁷⁵ J. B. Firth, *Trans. Faraday Soc.*, 1921, **16**, 434; *A.*, ii, 382.

⁷⁶ H. von Euler and A. H. Hedelius, *Arkiv Kem. Min. Geol.*, 1920, **7**, No. 31, 1; *A.*, ii, 490.

⁷⁷ M. Polányi, *Ber. Deutsch. Physik. Ges.*, 1916, **18**, 76; *A.*, 1916, ii, 474;

⁷⁸ G. Wiegner, J. Magasanik, and A. J. Virtanen, *Kolloid Z.*, 1921, **28**, 51; *A.*, ii, 244.

alkali nitrates are equivalent in all cases.⁷⁹ The adsorption increases with the atomic weight of the kation, and the same holds with nitrates of alkaline earths. Experiments with potassium and barium salts showed that the adsorption of halogen anions increases with the atomic weight. The variation with the kation is not considerable. With other salts, the order of adsorption varies with concentration. The negative adsorption of alkali haloids by wood charcoal has been measured.⁸⁰

The simultaneous adsorption of solvent and solute has been examined⁸¹ in the system benzene-iodine-charcoal. Equilibrium was attained through the vapour phase, and the temperature of the charcoal was kept above that of the liquid. The adsorption of benzene from iodine solutions was less than that from pure solvent. A comparison of the adsorption of water and alcohol by charcoal⁸² showed that the alcohol is adsorbed to nearly five times the extent of water. The result is not in agreement with Langmuir's opinion⁸³ that equal volumes should be adsorbed.

Osmosis.

An equation for the osmotic pressure of mixtures has been deduced.⁸⁴ The freezing-point depressions of pairs of non-electrolytes in concentrated solutions were determined separately and in admixture. The osmotic pressure of the mixture may be less or greater than the sum of the partial osmotic pressures. The facts are explained by van der Waals's theory of binary mixtures.

Donnan's theory of membrane equilibrium⁸⁵ has been applied⁸⁶ to the colloidal behaviour of proteins. Gelatin chloride solutions (P_H 3.5) containing various concentrations of sodium nitrate, in collodion bags, were placed in aqueous hydrochloric acid (P_H 3.0) containing similar concentrations of sodium nitrate. With increasing concentrations of neutral salt, the potential difference between the two solutions was depressed in the same proportion as the osmotic pressure of the gelatin chloride solution. The potential

⁷⁹ S. Odén and H. Andersson, *J. Physical Chem.*, 1921, 25, 311, A., ii, 438; S. Odén and E. W. Langelius, *ibid.*, 385; A., ii, 625.

⁸⁰ A. Pickles, *T.*, 1921, 119, 1278.

⁸¹ A. M. Bakr and J. E. King, *ibid.*, 454.

⁸² J. Driver and J. B. Firth, *ibid.*, 1126.

⁸³ *J. Amer. Chem. Soc.*, 1917, 39, 1848.

⁸⁴ R. Cernatesco, *Ann. Sci. Univ. Jassy*, 1920, 10, 259; *Chem. Zentr.*, 1921, iii, 199; A., ii, 576.

⁸⁵ *Z. Elektrochem.*, 1911, 17, 572; A., 1911, ii, 848; *T.*, 1911, 99, 1554; 1919, 115, 1313.

⁸⁶ J. Loeb, *J. Gen. Physiol.*, 1921, 3, 557, 667, 691; A., i, 368, 627; compare A., 1920, ii, 14, 234, 358, 476, 477, 602.

differences agreed with those calculated by Nernst's formula on the assumption that they were due to P_{II} . The effect of salts on the swelling or viscosity of gelatin chloride is similar. The results are explained by an unequal distribution of non-colloid ions on the two sides of the membrane. Proctor's expression ⁸⁷ for the Donnan equilibrium is verified. Electro-osmose in liquids of low conductivity has been studied ⁸⁸ by driving a liquid through a capillary tube and measuring the $E.M.F.$ A proportionality was found to exist between the $E.M.F.$ and the external pressure, as required by theory. A marked increase in the conductivity of a badly conducting liquid raises the potential difference at the surface of contact with the solid.

J. R. PARTINGTON.

⁸⁷ *T.*, 1914, **105**, 313; 1916, **109**, 307.

⁸⁸ W. Staszewski, *Krakau Anzeiger*, 1917, [A], 269; *Chem. Zentr.*, 1920; iii, 782; *A.*, ii, 13.

INORGANIC CHEMISTRY.

A GENERAL survey of the progress made during the year 1921 shows that whilst no new discovery of transcendent interest has been made, the great advances achieved in 1920 have been consolidated, and indeed in some cases have been still further extended. To those who keep pace with the rapid progress into virgin country by such pioneers as Rutherford, chemistry as she is to-day must present a fascination that never before was theirs. The reporter well remembers Sir Ernest saying that the mystery of the positive atomic nucleus by common consent must be left to a future generation to solve. By his newest work, however, he has already poached on the preserves of posterity, since a proof of the existence of H nuclei as satellites of a central nucleus would go far towards an elucidation of this mystery.

Apart from its bearing on Bohr's theory and the emission of spectra, this work leads to the conclusion that the atomic masses of the elements are not all exact whole numbers, as Aston's work has suggested. In the case of the elements with atomic masses given by $4N + 2$ and $4N + 3$, these atomic masses would be greater than whole numbers by 2×0.008 and 3×0.008 , respectively, owing to the fact that the two or three H nuclei are satellites of the inner nucleus and do not form an integral part of a closely-packed nucleus.

In view of the fact that a large number of the elements as we know them are mixtures of two or more isotopes, it is a very remarkable fact that the experimentally determined atomic weights should be constant. It has even been found that the atomic weights of terrestrial nickel and of nickel found in meteorites only differ by an amount that lies within the limit of experimental error, in spite of the fact that this element is a mixture of two isotopes in the ratio of 2 : 1. It is necessary to believe that in the genesis of this element, and indeed of all "impure" elements, the isotopes were always produced at the same time, at the same rate, and in the same place. The genetic processes of the isotopes of any one element must therefore have been closely connected so that one could not occur without the other, the products always being formed in constant ratio which probably was independent of

temperature and pressure, for it is impossible to believe that all the nickel which has yet been experimented with was formed under identical conditions of temperature and pressure.

Apart from this work on atomic theory and structure, there is much of great interest to be recorded on more stereotyped lines. Indeed, it may be said that the year's work is of great interest to all students of inorganic chemistry.

Atomic Theory.

Sir Ernest Rutherford has extended his investigations of the artificial disintegration of the light elements and has been able to draw certain conclusions, one of which would seem to be of very great importance.¹ It will be remembered that when the swiftly moving α -particles from radium-*C* pass through dry air or nitrogen, a few long-range particles are formed which can be detected by their scintillations on a zinc sulphide screen. These particles are bent in a magnetic field to about the same extent as swift H atoms of the same range, and there is little doubt that some of the nitrogen atoms are disintegrated by the intense collisions with the α -particles and that positively charged H atoms are liberated at a high speed. No such long-range particles are observed in oxygen or carbon dioxide. By improvements in the observing microscope, the counting of the scintillations has been made much easier and more certain. It has now been found that the particles from nitrogen have a much greater range of penetration than the corresponding H atoms from hydrogen. For example, using radium-*C* as a source of α -rays with a range in air of 7 cm., no H atoms from hydrogen can be detected after passing through screens of aluminium or mica of stopping power equivalent to 29 cm. of air. On the other hand, the maximum range of the particles from nitrogen corresponds with 40 cm. of air. This proves that these particles cannot be due to the presence of free hydrogen or hydrogen compounds, and also enables other elements besides nitrogen to be tested. If the scintillations are counted for absorptions greater than 29 cm. of air, the results are independent of the presence of hydrogen as an impurity.

The following table contains in the first column a list of the elements examined. The second column contains the materials actually used, the third column gives the number of scintillations observed per minute per milligram activity of the source at an absorption of 32 cm. of air, and the fourth column the maximum range of the particles :

¹ (Sir) E. Rutherford and J. Chadwick, *Phil. Mag.*, 1921, [vi], 42, 809; A., ii, 671.

Element.	Material.	No. of particles per min. per mg.	Maximum range of particles in cm. of air.
Lithium	Li_2O	—	—
Glucinum	GlO	—	—
Boron	B	0.15	ca. 45
Carbon	CO_2	—	—
Nitrogen	Air	0.7	40
Oxygen	O_2	—	—
Fluorine	CaF_2	0.4	over 40
Sodium	Na_2O	0.2	ca. 42
Magnesium	MgO	—	—
Aluminium	$\text{Al}, \text{Al}_2\text{O}_3$	1.1	90
Silicon	Si	—	—
Phosphorus	P (red)	0.7	ca. 65
Sulphur	S, SO_2	—	—

In addition to these, the following were examined—chlorine as MgCl_2 , potassium as KCl , calcium as CaO , titanium as Ti_2O_3 , manganese as MnO_2 , iron, copper, tin, silver, and gold in the form of metal foils. In no case were any particles observed of range greater than 32 cm. of air.

The effect of using α -particles of different velocities was investigated, the different ranges being 8.6, 7.0, 6.0, and 4.9 cm., respectively. The very interesting and important result was obtained that with a given element the particles observed increase rapidly in number and in velocity with the velocity of the α -particles.

It is reasonable to expect that the great majority of particles liberated from the various elements would be expelled in the direction of the α -particles, but in the case of aluminium it was found that the direction of escape is to a large extent independent of the direction of the α -particles. Nearly as many are expelled in the backward as in the forward direction, but the velocity in the backward is less than that in the forward direction.

There is little doubt that the particles are in all cases H atoms, which are released at different maximum speeds depending on the element and on the velocity of the incident α -particle. Of those so far examined, only those with atomic weights given by $4n + 2$ or $4n + 3$, where n is a whole number, give rise to H atoms. Elements of mass $4n$ like carbon, oxygen, and sulphur show no effect. This is clearly shown in the following table of elements which give H atoms:

Element.	Mass.	$4n + a$.
Boron	11	$2 \times 4 + 3$
Nitrogen	14	$3 \times 4 + 2$
Fluorine	19	$4 \times 4 + 3$
Sodium	23	$5 \times 4 + 3$
Aluminium	27	$6 \times 4 + 3$
Phosphorus	31	$7 \times 4 + 3$

This result receives a simple explanation on the assumption that the nuclei of these elements are built up of helium nuclei of mass

4 and of hydrogen nuclei. The importance of the helium nucleus as a unit of atomic structure in the heavy elements has been established by the study of radioactive changes. In order to account for the liberation of an H atom at high speed, it is natural to suppose that the H nuclei are satellites of the main nucleus. In a close collision, the α -particle is able to give sufficient energy to the satellite to cause its escape at high speed from the nucleus. The escape of the H atoms in all directions is readily explained on this supposition, since the directions will be determined by the angle at which the α -particles strike the orbit of the satellite. If the direction of the α -particles is tangential to the orbit, the H atom will be driven in the forward direction of the α -particles and away from the nucleus. If the H atom is driven towards the nucleus, it will describe an orbit close to the nucleus and escape in a backward direction. The difference in the velocity of the H atoms in the forward and backward directions is probably due to the fact that the nucleus has been set in motion in the direction of the α -particles before the close collision with the H satellite occurs. On this view, the relative velocity of the H atom and the residual nucleus is the same whether the H atom escapes in the backward or forward direction, but the actual velocity in the backward direction is less.

In the case of aluminium the law of conservation of energy does not hold unless the energy derived from the disintegration of the nucleus is taken into account. By making the three assumptions that the law of conservation of momentum is valid, that the resultant kinetic energy of the three bodies involved is the same whether the H atom is liberated in the forward or backward direction, and that the final energy of escape of the α -particle is not sensibly different in the two cases, it is possible to calculate the final distribution of energy between the three bodies involved. In the case of an α -particle with range of 7 cm., it is found that the total gain of energy of the parts after a collision is $0.45 \times$ the energy of the incident α -particle.

If the view is correct that the H nuclei are satellites of the central nucleus, the mass of the H satellite should not be very different from that of the free H nucleus, since the packing effect is absent. On the assumption that C = 12.00 and H = 1.008, the true atomic weight of nitrogen should be $12 + 2 \times 1.008 = 14.016$. Similar considerations should be applicable to the other elements from which H atoms can be liberated.

Reference must be made to some further work by Dr. Aston on the mass spectra of the elements.² The general method of the

² *Phil. Mag.*, 1920, [vi], **40**, 628; [vi], **42**, 140, 436; *A.*, 1920, ii, 718; 1921, ii, 474, 565. *Nature*, 1921, **107**, 520. *T.*, 1921, **119**, 677.

investigation was described in the Report for last year and it is only necessary to record the new results that have been obtained. Boron is a mixture of two isotopes of masses 10 and 11, the second of which is present in greater amount. The relative amounts of the two present, however, do not seem to agree well with an observed atomic weight as high as 10.9, but no evidence was found of the existence of an isotope with mass 12. Whilst fluorine was found to be a simple element, silicon consists of two isotopes 28 and 29, but the relative amounts of these two would give an atomic weight less than 28.3, and therefore in spite of the complete absence of experimental evidence there may be a third isotope of mass 30.

Bromine is an interesting case, because, instead of being almost a pure element of mass 80, it consists of an almost equal mixture of two isotopes with masses 79 and 81. Phosphorus and arsenic are both simple elements, and the experimental evidence is in favour of this also being the case with sulphur, in spite of the fact of the accepted value of the atomic weight.

The essential condition for satisfactory measurement of the atomic masses with the positive ray spectrograph is, of course, the existence of stable volatile substances which may either be the elements themselves or their compounds with other elements of known atomic mass. The majority of the elements do not satisfy this condition, and consequently, as elements less and less suitable are examined, the work becomes more difficult and the results either inconclusive or entirely negative. Thus no satisfactory measurements have as yet been made with selenium, tellurium, antimony, and tin. Iodine, on the other hand, which was used in the form of methyl iodide, gave very decided evidence of being a simple element of mass 127. As Dr. Aston says, this result is unexpected, since all the speculative theories of atomic evolution predict a complex iodine; thus Kohlweiler deduces five isotopes of masses 122, 124, 126, 128, and 130, and he also claims to have achieved a considerable separation of these by diffusion.

The earlier results obtained with xenon and chlorine have been revised. A purer specimen of xenon showed definite evidences of five isotopes of masses 129, 131, 132, 134, and 136, with distinct indications of a sixth component, 128, present in smaller quantity. It is possible also that there is a seventh isotope of mass 130. In the case of chlorine, strong confirmatory evidence has been obtained of the definite existence of the two isotopes 35 and 37, but the question of the third with mass 39 still remains in doubt.

It has been found possible by the use of an anode which was electrically heated by the current from a storage battery to observe the mass spectra of the alkali metals. In each case the anode was

coated with the salt of the metal. It was found that lithium is a mixture of two isotopes of masses 6 and 7, that sodium is a single element, that potassium and rubidium are mixtures of two isotopes, 39, 41, and 85, 87 respectively, and that caesium is a single element of mass 133. The atomic weight of caesium, 132.81, suggests the presence of a lighter isotope, but no evidence of this could be found, and if it exists it must be in very small amount.

Finally, by the use of nickel carbonyl, it has been found that nickel consists of two isotopes of masses 58 and 60 in the proportion of 2 : 1. This gives a value for the atomic weight of 58.67, which agrees closely with the accepted value. The whole of the observations may be tabulated as follows, the doubtful isotopes being enclosed within brackets.

Element.	Atomic number.	Atomic weight.	Minimum no. of isotopes.	Masses of isotopes in order of intensity.
H	1	1.008	1	1.008
He	2	3.99	1	4
Li	3	6.94	2	7, 6
B	5	10.9	2	11, 10
C	6	12.00	1	12
N	7	14.01	1	14
O	8	16.00	1	16
F	9	19.00	1	19
Ne	10	20.20	2	20, 22, (21)
Na	11	23.00	1	23
Si	14	28.3	2	28, 29, (30)
P	15	31.04	1	31
S	16	32.06	1	32
Cl	17	35.46	2	35, 37, (39)
A	18	39.88	(2)	40, (36)
K	19	39.10	2	39, 41
As	33	74.96	1	75
Br	35	79.92	2	79, 81
Kr	36	82.92	5	84, 86, 82, 83, 80, 75
Rb	37	85.45	2	85, 87
I	53	126.92	1	127
X	54	130.2	5 (7)	129, 132, 131, 134, 136, (128), (130 ?)
Cs	55	132.81	1	133
Hg	80	200.6	(6)	(197-200), 202, 204

Mention may also be made of measurements with a heated magnesium anode which establish the existence of three isotopes of masses 24, 25, and 26, which occur in the proportion of 6 : 1 : 1 and give an average atomic weight of 24.375.³

An interesting positive result in the partial separation of the isotopes of mercury has been announced.⁴ Two methods were employed, namely, evaporation and effusion. The density difference between the lightest and heaviest mercury was 0.49 per cent.,

³ A. J. Dempster, *Science*, 1920, **52**, 559; *A.*, ii, 402.

⁴ J. N. Brønsted and G. Hevesy, *Phil. Mag.*, 1922, [vi], **43**, 31.

which corresponds with a difference of 0.1 in the atomic weight of the element. The results of the experiments agree with the theory that the evaporation rate and effusion rate of the isotopes are inversely proportional to the square root of their molecular masses. Moreover, they conform with Aston's determinations of the atomic masses of the isotopes.

Atomic Weights.

Several papers have been published on the determination of atomic weights since the writing of the last Report. Of these, the following may be referred to.

Aluminium.—Aluminium bromide was synthesised from very pure bromine and the purest obtainable aluminium.⁵ It was digested three times in nitrogen at different temperatures, and fractionated by distillation twice in nitrogen and twice in a vacuum. The bromide was decomposed by water in such a way that the reaction occurred slowly, and the solution was precipitated by a weighed amount of pure silver. The silver bromide was collected and weighed. From the result of four closely agreeing analyses, the atomic weight was found to be 26.963. The modern evidence seems to show that the atomic weight of aluminium is really less, not more, than 27. The new value is distinctly nearer to a whole number than the old one.

Antimony.—Three preparations of antimony were combined with bromine,⁶ the resulting product was twice distilled under a pressure of 5–10 mm. as long as gaseous materials could be removed, and then distilled a third time under a pressure of less than 1 mm. into a series of small bulbs, which were sealed off as filled. The product was analysed for bromine in two ways; first, by finding the amount of silver equivalent to the sample in the usual way, secondly, by adding excess of silver nitrate, filtering, and weighing the silver bromide. Averaging the volumetric result for eleven samples with the gravimetric results for eight samples, the most probable atomic weight for antimony becomes 121.773.

Bismuth.—Bismuth triphenyl was prepared by the action of an excess of bismuth bromide on magnesium phenyl bromide.⁷ The product was decomposed by ice-water and distilled in a current of steam. The bismuth triphenyl was purified by crystallisation from absolute alcohol, and distillation, and for the purpose of atomic weight determination was left for ten hours over phosphoric oxide

⁵ T. W. Richards and H. Krepelka, *J. Amer. Chem. Soc.*, 1920, **42**, 2221; *A.*, ii, 48.

⁶ H. H. Willard and R. K. McAlpine, *ibid.*, 1921, **43**, 797; *A.*, ii, 405.

⁷ A. Classen and O. Ney, *Ber.*, 1920, **53**, [B], 2267; *A.*, ii, 119.

in a cathode-ray vacuum before weighing. It was converted into bismuth oxide by mixing weighed portions with pure oxalic acid in a porcelain crucible, moistening with pure alcohol, heating in an electric quartz muffle furnace, and finally ignited in a stream of oxygen. From ten determinations, the mean atomic weight was found to be 208.9967.

Reference was made in last year's Report to Hönigschmid's work, and a detailed account of this work has since been published.⁸ Two series of analyses of bismuth chloride and bismuth bromide are recorded. In each series, the atomic weight was determined by two independent methods, gravimetric estimation of the ratios $\text{BiCl}_3 : 3\text{AgCl}$ and $\text{BiBr}_3 : 3\text{AgBr}$, and nephelometric measurement of the silver haloid dissolved in the mother-liquor, and determination of the ratios $\text{BiCl}_3 : 3\text{Ag}$ and $\text{BiBr}_3 : 3\text{Ag}$ by gravimetric titration with the aid of the nephelometer. The mean value of the six most trustworthy series is $\text{Bi} = 208.997$ or in round numbers 209.00.

Classen and Ney's value has been re-calculated with the result that $\text{Bi} = 208.91$ which is 0.09 lower. Both values are decidedly higher than the international value.

Cadmium.—The atomic weight of cadmium has been re-determined by the electrolysis of anhydrous cadmium sulphate,⁹ it having been found that the hydrated salt generally contains a small amount of water above that required for the composition $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, and since such water cannot be removed, the hydrated salt is unsuitable for atomic weight determination. The weighed sulphate was dissolved in water and electrolysed, a weighed mercury cathode being used. As the result of eleven analyses, the value 112.409 was obtained for the atomic weight. The mean of the whole of the work of Baxter and his collaborators on the atomic weight of cadmium is 112.411.

Germanium.—The method employed was the conversion of potassium germanofluoride into potassium chloride by heating in hydrogen chloride.¹⁰ Very great care was taken in the purification of the germanium compounds before the double salt was prepared. The mean of seven determinations gave $\text{Ge} = 72.418$.

Lanthanum.—Two samples of lanthanum material were subjected to a prolonged series of crystallisations as double ammonium lanthanum nitrate, and the material finally obtained was shown to be entirely free from the other rare earths by spectroscopic examina-

⁸ O. Hönigschmid and L. Birckenbach, *Ber.*, 1921, **54**, [B], 1873; *A.*, ii, 646.

⁹ G. P. Baxter and C. H. Wilson, *J. Amer. Chem. Soc.*, 1921, **43**, 1230; *A.*, ii, 640.

¹⁰ J. H. Müller, *ibid.*, 1085; *A.*, ii, 456.

tion.¹¹ From six determinations, the ratio $\text{LaCl}_3 : 3\text{Ag}$ was found to give the atomic weight of 138·914. Seven determinations of the ratio $\text{LaCl}_3 : 3\text{AgCl}$ gave the atomic weight as 138·912. This is lower than the accepted value, 139·0, but since the presence of the usual companions of lanthanum, cerium, praseodymium, and neodymium, would raise the apparent atomic weight, this value must be regarded as a maximum.

Tellurium.—Pure tellurium dioxide was dissolved in pure aqueous sodium hydroxide and the tellurium estimated volumetrically either in alkaline or just acid solution.¹² The mean of twelve estimations in alkaline solution gave the value 127·8 for the atomic weight, and of nine estimations in acid solution the value 127·65.

Thulium.—The atomic weight of thulium has been determined from the ratio $\text{TmCl}_3 : 3\text{Ag}$ from three specimens of thulium.¹³ The purest fraction gave a value 169·44 for the atomic weight as a mean of three determinations, whilst the other two fractions, which contained neoytterbium, gave 169·66 and 169·90, respectively.

Zinc.—The atomic weight of zinc has been re-determined by means of the electrolytic estimation of the amount of zinc in zinc chloride.¹⁴ The carefully purified metal was converted into the bromide, and the purified salt fused in a current of chlorine. As a mean of eleven analyses of the chloride the value 65·372 was obtained, or, rejecting four relatively low values, 65·379. This value is in good agreement with recent determinations and indicates that the true atomic weight lies very close to 65·38.

Nickel.—A comparison has been made of the atomic weights of terrestrial and meteoric nickel, the method employed being the reduction of nickelous oxide with hydrogen.¹⁵ As a result of nine determinations with terrestrial material, a mean value of 58·70 was found, whilst three experiments with meteoric nickel gave 58·68. The difference is considered to be within the limits of experimental error.

Catalysis.

Yet another theory has been added to the list of those which have been put forward to explain the rusting of iron.¹⁶ According to this theory, iron is passive towards distilled water in the absence

¹¹ G. P. Baxter, M. Tani, and H. C. Chapin, *J. Amer. Chem. Soc.*, 1921, **43**, 1080; *A.*, ii, 454.

¹² P. Bruylants and G. Desmet, *Bull. Soc. chim. Belg.*, 1914, **28**, 264; *A.*, ii, 448.

¹³ C. James and O. J. Stewart, *J. Amer. Chem. Soc.*, 1920, **42**, 2022; *A.*, 1920, ii, 759.

¹⁴ G. P. Baxter and J. H. Hodges, *ibid.*, 1921, **43**, 1242; *A.*, ii, 639.

¹⁵ G. P. Baxter and L. W. Parsons, *ibid.*, 507; *A.*, ii, 338.

¹⁶ J. A. N. Friend, *T.*, 1921, **119**, 932.

of a catalyst and passes into solution, but only with extreme slowness, owing to the traces of electrolytes that are present. The iron passes into solution as ferrous ions, but is rapidly converted into the sol of ferrous hydroxide. This sol is oxidised by the dissolved oxygen to the sol of a higher hydroxide, which now acts catalytically, by oxidising metallic iron with relatively great rapidity and simultaneously being reduced to the lower hydroxide, only to be oxidised again by the dissolved oxygen. In other words, the sol acts as an oxygen carrier.

A number of experimental results are given in support of this theory. In the first place, if pure metallic iron is suspended in a stream of water, the amount of corrosion increases to a maximum as the velocity of the stream is increased. With further increase in the velocity of the water, the amount of corrosion decreases to a minimum. There was, however, a distinct loss in weight of the iron even when the velocity was 30,000 feet an hour, but this is attributed to mechanical erosion. Somewhat analogous observations were made of the potential difference between iron and platinum wires immersed in dilute solutions of electrolytes at rest and in motion. Slight movement increases the potential difference, but a maximum is soon attained, after which an increase in velocity causes the potential difference to fall to a constant value. These results are interpreted to mean that the rapidly moving water sweeps away the colloid from the surface of the iron.

If the suggested theory is correct, then the inhibiting effect of dissolved salts on the corrosion of iron should be proportional to the coagulating power of the salts on hydrosols. Some measurements of the effect of solutions of certain salts on corrosion show decreases which are comparable with their precipitating powers towards colloidal ferric hydroxide. Confirmatory evidence is also found in the inhibiting action on the corrosion of protective colloids, of colloid poisons, and of the β - and γ -rays from radium.

It is further suggested that this theory is of more general application, since many reactions which have hitherto been ascribed to ions may possibly be explained more readily on the autocolloid, catalytic theory. Many so-called catalysts, which are known to be chemically inert, may act by rendering possible the existence of a colloid catalyst formed from the reacting substances themselves. They are not, therefore, true catalysts in the sense of actually taking part in the reactions themselves, but may be termed secondary catalysts. For instance, the addition of dry benzene causes instant combination between perfectly pure and dry ammonia and hydrogen chloride. It is quite in accord with the behaviour of benzene, however, to suppose that it facilitates the formation and stabilisation

of a colloidal form of ammonium chloride, which catalytically assists the union of the remaining ammonia and hydrogen chloride.

Whilst not necessarily denying the correctness of Dr. Friend's theory of the corrosion of iron, the reporter feels that his proposed application to such cases as ammonia and hydrogen chloride is open to criticism, mainly for the reason that it offers no explanation. The statement that the known catalytic effect of benzene on a mixture of ammonia and hydrogen chloride is due to the fact that it forms another catalyst does not advance our knowledge. The essential underlying factor in all reaction is energy, and the rôle of the catalyst is to supply the necessary energy to the catalyte. Every reaction consists of three stages, and the first of these is the conversion of the reactant molecules from their normal and non-reactive phase into the reactive phase, a change which requires the supply of energy to the molecules. The second stage is the rearrangement of the atoms whereby new compounds are produced, and it is this stage, and this stage only, which is expressed by the chemical change of the reaction. The third stage is the conversion of the newly synthesised molecules into their normal and non-reactive phase. The second and third stages are accompanied by an evolution of energy, and the observed heat of the reaction is the difference between the sum of the two amounts of energy evolved in the second and third stages and that absorbed in the first stage.

The energy necessary for the first stage may be gained by exposing the reactant molecules to heat or light, when the reaction is called thermal or photochemical. The necessary increment of energy may also be supplied by a material catalyst, the word catalyst being used in the broadest sense. In whatever way the catalyst behaves, the fact remains that it functions as a supplier of energy to the reactant molecules, whereby they are converted from the non-reactive to the reactive phase.

It is true that many reactions may be said to proceed without the addition of a specific catalyst, but this is simply due to the fact that the reactant molecules have already been brought into their reactive phases by the use of a solvent, the solvent, of course, being the catalyst. Then, again, there is the phenomenon of autocatalysis, when the velocity of a reaction, at first small, increases up to a maximum. When the second and third phases of the reaction are taking place, energy is radiated, and this energy can be re-absorbed by the surrounding reactant molecules, with the result that more of these are activated and the velocity increases to a maximum defined by the amount of the radiated energy that is re-absorbed. This has been proved to take place in the case of the photochemical union of

hydrogen and chlorine, and in the photosynthesis of formaldehyde and sugars from carbon dioxide and water.

To take the case quoted of ammonia and hydrogen chloride, these gases, when pure and dry, exist in their non-reactive phases, and the catalyst, whether it be water vapour or benzene, supplies energy to the molecules so that they are converted into their reactive phases, which instantly combine to form ammonium chloride. The statement that one catalyst acts by producing another is of little use, for, if explanation is sought of the rise in velocity observed after the reaction has commenced, it is to be found in the re-absorption by the reactant molecules of the energy radiated in the reaction between a few of these.

It may be noted that the very interesting observation made by Sugden can be explained very readily on this theory.¹⁷ The activity of nascent hydrogen is by no means necessarily due to its dissociation into free atoms. The normal, non-reactive hydrogen molecule can be rendered active for certain reactions by an amount of energy which is smaller than that required to dissociate it into atoms. This is exemplified by the activation of a portion of the hydrogen when three volumes of this gas are exploded with one volume of oxygen.¹⁸ The residual gas reduces alkaline potassium permanganate to manganate, indigotin in alkaline solution to indigo-white, ferric chloride to ferrous chloride, potassium nitrate to potassium nitrite, arsenious acid to arsine, potassium perchlorate to potassium chloride, etc. A similar explanation is applicable to the active form of hypophosphorous acid.¹⁹

In their important paper on the catalytic oxidation of ferrous salts, Thomas and Williams²⁰ recognise that neither intermediate compound formation nor adsorption alone is capable of explaining catalysis. The key to the problem is the transference of energy to the catalyte by way of the intermediate compound or of adsorption. Again, in the cases of heterogeneous catalysis by metals, it follows from this theory that the activation by the catalyst cannot extend to more than a molecular layer of the catalyte. The experimental evidence supports this conclusion very strongly, and the particular case of palladium is dealt with under Group VIII.

In conclusion, two questions may be asked as regards Dr. Friend's theory of the corrosion of iron, which in spite of their very obvious nature do not seem to have been dealt with in his paper. The first of these is, Why is rust formed and not a solution of ferric

¹⁷ S. Sugden, *T.*, 1921, **119**, 233.

¹⁸ Y. Venkatramaiah, *Nature*, 1920, **106**, 46.

¹⁹ A. D. Mitchell, *T.*, 1921, **119**, 1266.

²⁰ R. Thomas and E. T. Williams, *ibid.*, 749.

hydroxide sol? The second question is, Does iron rust with greater rapidity in a solution of ferric hydroxide sol?

Group I.

The properties of pure hydrogen peroxide have been investigated and a method given for its preparation.²¹ Three per cent. hydrogen peroxide, obtained from barium peroxide, is concentrated to 30 per cent. by means of a sulphuric acid concentrator.²² It is then distilled at very low pressure to remove the non-volatile impurities. A further concentration by the sulphuric acid concentrator at 0° raises the concentration to 90 per cent., and the final product, 100 per cent. hydrogen peroxide, is obtained by fractional solidification and melting. The pure substance is found to have the following physical properties: m. p. -1.70° , density of liquid at -0.53° 1.4638, association factor 3.48, specific heat between 0° and 18.5° 0.5730, latent heat of fusion 73.91 cal. Hydrogen peroxide is very slightly soluble in ether, it dissolves many normal salts, and it attacks glass. Freezing-point determinations of solutions of hydrogen peroxide in water show that only one compound, $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$, exists with melting point -51° .²³

Some work has been done on the hydrides of the alkali metals. In the case of lithium hydride, it would seem that the substance possesses the properties of a salt.²⁴ Electrolysis of the compound gives lithium at the cathode and, apparently, hydrogen at the anode, this being the first observed instance of hydrogen functioning as a negatively charged ion. The following constants were determined: density 0.816, molecular volume 9.77, heat of formation $21,600 \pm 250$ cal., $\text{Li} + \text{H}_2\text{O} = \text{LiOH} + \text{H} + 52,723 \pm 200$ cal., $\text{LiH} + \text{H}_2\text{O} = \text{LiOH} + \text{H}_2 + 31,110 \pm 50$ cal.

Pure sodium hydride can best be prepared by leading a rapid stream of hydrogen directly on to the surface of the metal at such a temperature that a yellow glow is produced.²⁵ The temperature must be above 350° , when the sodium hydride is carried away as a white smoke, which is precipitated electrically and filtered through glass wool. Potassium hydride can be obtained by leading the gas into the metal at 350° . The reaction in each case is facilitated by the presence of metallic calcium.

Rubidium and caesium hydrides were prepared by heating a

²¹ O. Maass and W. H. Hatcher, *J. Amer. Chem. Soc.*, 1920, **42**, 2548; *A.*, ii, 106.

²² O. Maass, *ibid.*, 2571; *A.*, ii, 104.

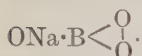
²³ O. Maass and O. W. Herzberg, *ibid.*, 2569; *A.*, ii, 106.

²⁴ K. Moers, *Z. anorg. Chem.*, 1920, **113**, 179; *A.*, ii, 200.

²⁵ F. Ephraim and E. Michel, *Helv. Chim. Acta*, 1921, **4**, 762; *A.*, ii, 638.

mixture of their carbonates with metallic magnesium in hydrogen at 650° for five days and at 580—620° for three days, respectively. The stability of these hydrides decreases from sodium to caesium.

Some doubt has been thrown on the correctness of the formula $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ for sodium perborate, it being stated that the composition is more correctly represented by $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$.²⁶ The salt, after partial dehydration at 50—55°, loses more water at 120° in a vacuum and the residue consists chiefly of $(\text{NaBO}_2)_2\text{O}_2$. This substance loses oxygen on treatment with water and has properties which differ from those of NaBO_3 , and it is concluded that a substitution product of H_2O_2 exists with constitution



Three crystalline hydrates of disodium hydrogen phosphate are known with $12\text{H}_2\text{O}$, $7\text{H}_2\text{O}$, and $2\text{H}_2\text{O}$, respectively. The dihydrate can readily be prepared by boiling the finely-powdered dodecahydrate with ethyl alcohol, whilst the heptahydrate can be obtained by fusing the appropriate mixture of the dodecahydrate and dihydrate and cooling.²⁷ The following transition temperatures have been determined: $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O} - \text{Na}_2\text{HPO}_4$, 94·97°; $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O} - \text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, 48·09°; $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} - \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, 35·0°. In addition to this, sharp breaks were observed in the heating and cooling curves for the dodecahydrate at 29·6°, due to a change of phase in this substance. Two forms of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ exist, of which one is stable between 29·6° and 35·0° and the other is stable below 29·6°. The existence of these two forms has been confirmed by solubility measurements.

It has been recorded that by the action of dry nitrogen peroxide on pure copper powder the compound Cu_2NO_2 is produced. Some further work has now been carried out on this reaction, as the result of which it has been proved that this compound does not exist.²⁸ The copper powder was prepared by reduction of copper oxide with hydrogen and by reduction of hydrated cuprous oxide with carbon monoxide. The cuprous oxide was obtained by pouring a solution of pure cuprous chloride in dilute hydrochloric acid into a dilute solution of sodium hydroxide. The product, after being dried over phosphoric oxide in a vacuum, was found to be $4\text{Cu}_2\text{O} \cdot \text{H}_2\text{O}$.

When the copper powder was allowed to remain in contact with nitrogen peroxide, absorption took place, but no stoichiometric relation could be found between the weight of the copper and the

²⁶ F. Foerster, *Z. angew. Chem.*, 1921, **34**, 354; *A.*, ii, 506.

²⁷ D. L. Hammick, A. K. Goadby, and H. Booth, *T.*, 1921, **119**, 1589.

²⁸ H. V. Tartar and W. L. Semon, *J. Amer. Chem. Soc.*, 1921, **43**, 494; *A.*, ii, 336.

increase in weight. Analysis of the product showed that the atomic ratio of nitrogen to oxygen was 1 : 3. Moreover, the product loses weight on being exposed to air due to the evolution of nitric oxide or nitrogen peroxide. When the product is treated with water, 90 per cent. of the nitrogen is found in the form of nitrate and 10 per cent. as nitrite. It is suggested that the reaction consists in the formation of anhydrous cuprous nitrate on the surface of the copper.

Group II.

A description has been given of the preparation of the yellow higher oxides of calcium and barium, and it is believed that these are the tetroxides.²⁹ The calcium compound may be prepared by gently warming calcium peroxide octahydrate with five to six times its weight of pure hydrogen peroxide (30 per cent.) until a vigorous evolution of oxygen occurs. The mixture is allowed to cool until the evolution of gas subsides, and the warming and cooling are repeated until practically no more gas is evolved. The precipitate is washed successively with water, alcohol, and ether, and dried. The product has a bright yellow colour and can be heated at 130° without change. It dissolves in acid with a brisk evolution of oxygen mixed with a small amount of carbon dioxide and with the formation of hydrogen peroxide. The evolved oxygen is inactive, since bromine is not liberated when the evolution takes place in an acidified solution of potassium bromide. The only known types of substance which evolve inactive oxygen are the oxyhydroxides, for example, $(\text{KOH})_2\text{O}_2$, and the tetroxides, for example, K_2O_4 . The stability of the calcium oxide towards heat excludes the first, so that in all probability it is calcium tetroxide, CaO_4 . As judged by the amount of oxygen evolved, this substance is present to the extent of 8.7 per cent.

Barium tetroxide is much less stable than the calcium compound. The substance $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$ can only be preserved for a short time at temperatures below 0°. At the atmospheric temperature, it rapidly becomes yellow owing to the formation of the tetroxide, and the colour increases in intensity during twenty-four to thirty-six hours, after which it disappears almost completely within four or five days, the complete reaction being $2\text{BaO}_2 \cdot \text{H}_2\text{O}_2 = 2\text{BaO}_2 \cdot \text{H}_2\text{O} + \text{O}_2$. If the highly coloured preparations are dissolved in acid, inactive oxygen is evolved corresponding in amount with about 8 per cent. of barium tetroxide in the best preparations. It was found impossible to prepare purer specimens of the tetroxides owing to the readiness with which the products decomposed in the presence of water.

²⁹ W. Traube and W. Schulze, *Ber.*, 1921, 54, [B], 1626; *A.*, ii, 548.

Some work has been carried out on the crystallisation of calcium and magnesium carbonates with the view of explaining the natural formation of these salts and of dolomite.³⁰ In the presence of magnesium sulphate, calcium carbonate crystallises at 20° from water saturated with carbon dioxide only in the form of aragonite; 0.9 per cent. of magnesium sulphate is sufficient to inhibit the appearance of calcite. It was stated by Vaubel³¹ that aragonite and calcite differ in that the former contains traces of a basic carbonate, but this has now been shown experimentally to be incorrect.

Saturated solutions of magnesium hydrogen carbonate deposit between 65° and the boiling point a basic carbonate, $4\text{MgO} \cdot 3\text{CO}_2 \cdot 6\text{H}_2\text{O}$, in the form of slender needles. Between 65° and 55°, the basic carbonate separates, mixed with the trihydrate, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$; below 55°, the trihydrate alone is formed down to about 6°, and at 2° the unstable pentahydrate is formed.³² All attempts to crystallise magnesite fail, and it is concluded that this mineral is of marine origin.

Numerous attempts were made to obtain synthetic dolomite by crystallisation of calcium and magnesium carbonates under different conditions, but without success. It is suggested that mixtures of the composition of dolomite are formed from sea-water, the mechanism of the recrystallisation as dolomite being unknown.

Various methods for the purification of mercury which has become contaminated with other metals by use in the laboratory have been suggested from time to time. It has been shown that distillation alone is not effective, and the treatment with nitric acid or mercurous nitrate solution is often of very little use. It is now claimed³³ that the most efficient method is to heat the metal at 150° in a flask while passing a current of air through it by means of a glass tube extending about 1 cm. below the surface. After several hours, the metal is filtered from the scum and again treated by the same method. The process is repeated until no further scum forms, after which the filtered metal is distilled in a vacuum from an ordinary fractionating flask.

The purification of impure mercury by treatment with air is not in any way new, and the novelty consists in the heating at 150°. It may be pointed out that a very essential necessity in all methods involving the treatment with air is the complete absence of dust.

Two methods have been described for the preparation of mercuric azide in a form which is less sensitive than the ordinary form.³⁴

³⁰ H. Leitmeier, *Jahrb. Min.*, 1916, *Beil. Bd.*, **40**, 655; *A.*, ii, 112.

³¹ *J. pr. Chem.*, 1912, [ii], **86**, 366; *A.*, 1912, ii, 1180.

³² H. Leitmeier, *Z. Kryst. Min.*, 1909, **47**, 104; *A.*, 1910, ii, 49.

³³ C. Harries, *Z. angew. Chem.*, 1921, **34**, 359; *A.*, ii, 552.

³⁴ A. Stettbacher, *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 211; *A.*, ii, 48.

It appears that the sensitivity is greatly dependent on the crystalline form. Thus, by mixing concentrated solutions of sodium azide and mercuric nitrate, mercuric azide is precipitated as a powdery mass. The salt as thus prepared is even less sensitive than lead azide, but it is converted into the highly sensitive form by recrystallisation.

Crystalline compounds of mercurous oxide with ammonia and sulphur dioxide have been prepared by the action of sulphur dioxide on the precipitate obtained from mercuric chloride and excess of ammonia.³⁵ The precipitate dissolves and the compounds separate when the solutions are evaporated under reduced pressure. If sulphur dioxide is first added and then ammonia, the compounds $\text{Hg}(\text{SO}_3 \cdot \text{NH}_4)_2$ and $\text{HgCl}(\text{SO}_3 \cdot \text{NH}_4)$ are produced. Excess of ammonia gives the compounds $\text{Hg} \cdot \text{SO}_3 \cdot \text{NH}_3$ and $\text{Hg}(\text{SO}_3 \cdot \text{NH}_4)\text{OH}$. In the presence of large amounts of ammonium chloride the compound $\text{NH}_3\text{Cl} \cdot \text{Hg} \cdot \text{SO}_3 \cdot \text{NH}_4$ is formed, which is converted by potassium hydroxide into $\text{Hg}_2\text{O} \cdot \text{SO}_3 \cdot \text{NH}_3$.

Group III.

Boron nitride has been prepared in quantity by leading a mixture of boron trichloride vapour and ammonia through an intensely heated tube.³⁶ Difficulty was caused by the voluminous nature of the nitride, but this was overcome by the use of a quartz tube which was electrically heated in zones. The yield was 80–85 per cent., and the nitride was obtained as a colourless powder, the reactivity of which depends on the temperature at which the reaction is carried out. At 800° , a very voluminous product is obtained which, after exposure to the atmosphere, gives some ammonia. The product obtained at much higher temperatures is more stable in air.

A convenient method has been given for the preparation of calcium arsenide which can be employed for the formation of hydrogen arsenide.³⁷ A neutral diluent such as sand or calcium arsenide from a previous preparation is added to the extent of 50 per cent. by weight to a mixture of powdered arsenic and calcium filings. The whole is placed inside a sheet-iron container enclosed within a second vessel. The reaction is started by means of a magnesium–potassium chlorate mixture and steadily proceeds throughout the entire mass. There is no flame and very little arsenious oxide is formed.

The resulting calcium arsenide, on treatment with water or acids,

³⁵ O. Ruff and E. Kröhnert, *Z. anorg. Chem.*, 1920, **114**, 203; *A.*, ii, 202.

³⁶ F. Meyer and R. Zappner, *Ber.*, 1921, **54**, [B], 560; *A.*, ii, 329.

³⁷ H. Thoms and L. Hess, *Ber. Deut. Pharm. Ges.*, 1920, **30**, 483; *A.*, ii, 110.

gives hydrogen arsenide containing 14 per cent. by volume of hydrogen. Aqueous solutions of the gas undergo rapid decomposition with formation of colloidal arsenic, and the reaction may be followed by titration with *N*/100-iodine solution. At first, the hydride is oxidised according to the equation $\text{AsH}_3 + 3\text{I}_2 + 3\text{H}_2\text{O} = \text{H}_3\text{AsO}_3 + 6\text{HI}$. After rendering the solution alkaline by the addition of potassium hydrogen carbonate, the normal oxidation to arsenic acid takes place.

An acid fluoride of thallium, H_2TlF_3 , is obtained by dissolution of thallium in hot dilute hydrogen fluoride and evaporation of the solution to dryness.³⁸ The salt loses hydrogen fluoride on being heated and forms with water acid solutions, which, however, do not attack glass. The neutralisation curve shows that two types of complex salts exist, for example, KHTlF_3 and K_2TlF_3 .

Group IV.

An important paper has appeared on the preparation of the trithiocarbonates and perthiocarbonates of the alkali and alkaline earth metals.³⁹ The general method of preparation was the addition of the requisite amount of carbon disulphide to alcoholic solutions of either the hydrosulphides or the disulphides of the metals. These solutions were obtained by the method described by Rule and Thomas. After the carbon disulphide had been added, the thiocarbonates separated after dilution with ether. The operations were carried out in an atmosphere of hydrogen, since the salts readily decompose in the presence of moist air or carbon dioxide. Sodium trithiocarbonate, $\text{Na}_2\text{CS}_3 \cdot \text{H}_2\text{O}$, forms very deliquescent needles with a pinkish-yellow colour. They give a distinctly red solution in water, which is stable if oxygen and carbon dioxide are rigidly excluded. The perthiocarbonate, $\text{Na}_2\text{CS}_4 \cdot 3\text{H}_2\text{O}$, separates as brownish-yellow needles and is very deliquescent. It readily dissolves in water to a distinctly yellow solution. The heats of formation of sodium trithiocarbonate and sodium perthiocarbonate in alcoholic solution were found to be 5700 and 8550 cals., respectively.

The following salts were also prepared, K_2CS_3 ; $2\text{K}_2\text{CS}_4 \cdot \text{H}_2\text{O}$;
 $3\text{Ca}(\text{OH})_2 \cdot \text{CaCS}_3 \cdot 9\text{H}_2\text{O}$; $\text{Ca}(\text{OH})_2 \cdot \text{CaCS}_3 \cdot 2\text{H}_2\text{O}$;
 $2\text{Ca}(\text{OH})_2 \cdot \text{CaCS}_4 \cdot 8\text{H}_2\text{O}$; $\text{SrCS}_3 \cdot 4\text{H}_2\text{O}$; $\text{SrCS}_4 \cdot 8\text{H}_2\text{O}$; BaCS_3 ;
 $(\text{NH}_4)_2\text{CS}_3$; $(\text{NH}_4)_2\text{CS}_4$; $(\text{NH}_4)_2\text{CS}_4 \cdot \text{H}_2\text{O}$.

Reference may be made to some further work on the hydrides of silicon and their derivatives.⁴⁰ Attempts were made to synthesise

³⁸ Barlot, *Compt. rend.*, 1920, **171**, 1143; *A.*, ii, 113.

³⁹ E. W. Yeoman, *T.*, 1921, **119**, 38.

⁴⁰ A. Stock and K. Somieski, *Ber.*, 1921, **54**, [B], 524; *A.*, ii, 330.

disilane by the action of the alkali metals on monochlorosilane, but the results obtained were unexpected.

Monochlorosilane reacts readily with potassium at the ordinary temperature, but the metal becomes coated with a protective layer which speedily inhibits the reaction. At 300° , the reaction is complete, the products being silicon, potassium hydride, potassium chloride, and hydrogen. When allowed to remain in contact with potassium-sodium alloy for a month, monochlorosilane gave an incomplete reaction. The chief volatile product was monosilane, whilst disilane could only have been present in traces. When sodium amalgam was used, the chief product again was monosilane mixed with a small amount of hydrogen, but in this case the presence of disilane in small quantity was definitely established. Disilane undergoes slow decomposition in the presence of sodium-potassium alloy or of sodium amalgam to give hydrogen and monosilane. It may be noted that methyl chloride behaves similarly to monochlorosilane towards sodium amalgam, since it gives methane and ethane. Dichloromonosilane is converted by sodium amalgam into monosilane and hydrogen.

Chlorosilane and ammonia⁴¹ react at the ordinary temperature quantitatively to give ammonium chloride and trimonosilylamine, $\text{N}(\text{SiH}_3)_3$. The latter is a spontaneously inflammable liquid with m. p. -105.6° , b. p. 52° , and density 0.895. It is stable in the absence of air and is vigorously decomposed by water according to the equation $\text{N}(\text{SiH}_3)_3 + 6\text{H}_2\text{O} = 3\text{SiO}_2 + \text{NH}_3 + 9\text{H}_2$. The vapour density corresponds with the simple formula, $\text{N}(\text{SiH}_3)_3$, and the substance does not combine with hydrogen chloride or monochlorosilane.

By the action of an excess of ammonia on monochlorosilane, the initial product obtained is chiefly dimonosilylamine, $\text{NH}(\text{SiH}_3)_2$, which is probably mixed with the corresponding tri- and monoamines. The diamine is only comparatively stable and decomposes gradually according to the equation $\text{NH}(\text{SiH}_3)_2 = \text{SiH}_4 + \text{SiH}_2\text{:NH}$. The last compound cannot exist in the unimolecular form and condenses rapidly to the solid polymeride, $(\text{SiH}_2\text{:NH})_x$. A second reaction also takes place to a smaller extent with evolution of ammonia, $\text{SiH}_3\text{:NH}_2 \rightarrow \text{NH}(\text{SiH}_3)_2 \rightarrow \text{N}(\text{SiH}_3)_3$, with the result that the composition of the final residue corresponds with that of a mixture of $(\text{SiH}_2\text{:NH})_x$ and $\text{N}(\text{SiH}_3)_3$.

Between dichlorosilane and excess of ammonia the following reaction takes place at the ordinary temperature, $\text{SiH}_2\text{Cl}_2 + 3\text{NH}_3 = 2\text{NH}_4\text{Cl} + \text{SiH}_2\text{:NH}$.

The polymeride, $(\text{SiH}_2\text{:NH})_x$, is a white substance resembling

⁴¹ A. Stock and K. Somieski, *Ber.*, 1921, **54**, [B], 740; *A.*, ii, 399.

silicic acid, and the value of x is certainly very high, since when the compound is produced in benzene solution, $x = 7-8$. When the benzene solution is evaporated, a viscous liquid is obtained which only slowly passes into the solid and more highly polymerised conditions.

The behaviour of the silylamines when treated with hydrogen chloride is very remarkable, because they are smoothly and quantitatively transformed into monochlorosilane and ammonium chloride.

When calcium silicide was carefully treated with cold dilute alcoholic hydrochloric acid in the dark, a white, solid substance was obtained together with a certain amount of hydrogen.⁴² The white substance has the constitution $\text{Si}_2\text{H}\cdot\text{OH}$, and to it has been given the name of oxydisilin. It is a powerful reducing agent and is converted by means of bromine to silical bromide, Si_2OHBr . This substance is hydrolysed by water to silical hydroxide, a red compound which combines with strong acids to form salts that are yellow to red in colour. The silical compounds are all powerful reducing agents and they are decomposed by alkalis to form silica with evolution of hydrogen.

It has generally been believed that the coloured compounds obtained by the action of hydrogen peroxide on titanate salts are derivatives of the oxide, TiO_3 . From estimations of the active oxygen it appears that these compounds are really complexes of hydrogen peroxide and pertitanate salts derived from the peroxide, Ti_2O_5 .⁴³ The complex double potassium salt, $\text{K}_2\text{SO}_4\cdot\text{TiOSO}_4$, was prepared, and when the salt was dissolved in ice-cold water and alcohol added, the clear liquid decanted from the precipitate was found to contain hydrogen peroxide. The addition of alcohol to a solution prepared by pouring equimolecular quantities of potassium sulphate and titanyl sulphate into an excess of hydrogen peroxide gave a precipitate of the hydrated peroxide, $\text{Ti}_2\text{O}_5\cdot x\text{H}_2\text{O}$.

Some doubt has been thrown on the usually accepted explanation of the existence of the various forms of lead monoxide. This explanation is due to Ruer,⁴⁴ who stated that the forms are different allotropic modifications. It is now suggested that there is a much closer relationship between the forms, and, indeed, that the difference between them is due to variations in the size of the particles.⁴⁵ The red form of the oxide consists of particles, 3μ to 5μ , which, on being heated at 700° and then cooled, give yellow agglomerates, 10μ to 20μ . These easily break down under pressure to particles smaller

⁴² H. Kautsky, *Z. anorg. Chem.*, 1921, **117**, 209; *A.*, ii, 505.

⁴³ M. Billy, *Compt. rend.*, 1921, **172**, 1411; *A.*, ii, 456.

⁴⁴ R. Ruer, *Z. anorg. Chem.*, 1906, **50**, 265; *A.*, 1906, ii, 755.

⁴⁵ S. Glasstone, *T.*, 1921, **119**, 1689.

than those of the original red form, 0.7μ to 1.5μ . The reddish-brown preparations consist of particles of the same order of magnitude as the finer particles of the yellow forms. All the forms give a brown powder on being ground in a mortar, the particles of which are uniformly 0.7μ in diameter.

It is to be expected therefore that differences in solubility should be found depending on the size of the particles. The red form should have the lowest solubility and the reddish-brown forms should give higher values. This was proved to be the case by determination of the solubility of the various forms in a *N*-solution of sodium hydroxide free from carbonate.

The author makes no reference to the fact that the yellow form of lead monoxide is converted into the red form on exposure to light. This would lead to the conclusion that the difference is not only concerned with the size of the particles, but that there is a difference of energy content, at any rate between the yellow and red forms.

Group V.

Anhydrous ammonia and anhydrous chlorine react together to form nitrogen chloride and ammonium chloride, and the quantities that react do not change even when the relative proportions of the two reactants are varied between wide limits.⁴⁶ There is little or no reaction between chlorine and the solid ammonium chloride which is formed. A considerable proportion of the nitrogen chloride at first formed decomposes into nitrogen and chlorine, either directly or by interaction with ammonia.

Nitrogen chloride is quantitatively converted by dry hydrogen chloride into ammonium chloride, the action taking place in the presence or absence of an inactive solvent.⁴⁷ The reaction, therefore, is not one of hydrolysis and probably consists in the initial formation of trichloro-ammonium chloride, NCl_3HCl , which loses one positive atom and one negative atom of chlorine, the addition of hydrogen chloride and loss of chlorine taking place three times in succession. The formation of nitrogen chloride by the action of chlorine on an ammonium salt would seem to be the reverse of this reaction. For the preparation of nitrogen chloride ammonium sulphate is more suitable than ammonium chloride. Hypochlorous acid is preferable to free chlorine, because the use of the latter leads to the formation of some chloroamine and dichloroamine along with the nitrogen chloride.

Attempts were made to cause direct combination between

⁴⁶ W. A. Noyes and A. B. Haw, *J. Amer. Chem. Soc.*, 1920, **42**, 2167; *A.*, ii, 42.

⁴⁷ W. A. Noyes, *ibid.*, 2173; *A.*, ii, 42; *ibid.*, 1921, **43**, 1774.

nitrogen and chlorine by passing a mixture of the two gases through the flaming arc and also through an efficient ozoniser. No measurable combination took place, nor was there any reaction when active nitrogen was passed over chlorine at -190° .

An investigation has been made of the conditions under which the various compounds of ammonia and carbonic acid may be prepared from solutions of these two components.⁴⁸ Five compounds were obtained, and of these only one, $\text{NH}_4\cdot\text{HCO}_3$, forms a true equilibrium in which the ratio between CO_2 and NH_3 is the same in the solution and in the solid phase. It was found that the double salt, $2\text{NH}_4\cdot\text{HCO}_3, (\text{NH}_4)_2\text{CO}_3, \text{H}_2\text{O}$, crystallises from solutions containing NH_3 and CO_2 in the ratio 4 : 5. Normal ammonium carbonate may be prepared by adding 395 grams of ammonium hydrogen carbonate to 150 grams of water and 333 grams of ammonia solution (25 per cent.) and passing in ammonia under an increased pressure of 0.2 atm. The mixture is warmed at 40° until solution is complete, when, on cooling to 10° , the normal salt separates.

Solutions were prepared by dissolving each of the above salts and ammonium carbamate in aqueous ammonia of different concentrations, and these solutions were cooled to the temperature required. The range of temperature was from 0° to 60° , and the following solid phases were identified between 0° and 33° — $\text{NH}_4\cdot\text{HCO}_3$; $2\text{NH}_4\cdot\text{HCO}_3, (\text{NH}_4)_2\text{CO}_3, \text{H}_2\text{O}$; $(\text{NH}_4)_2\text{CO}_3$; $\text{NH}_4\cdot\text{HCO}_3, \text{NH}_4\cdot\text{CO}_2\cdot\text{NH}_2$; $\text{NH}_4\cdot\text{CO}_2\cdot\text{NH}_2$. Of these, the normal carbonate and the two double salts have a limited temperature range of stability. Between 33° and 60° , no further change was observed.

A convenient method for the storage of ammonia has been described⁴⁹ which is based on the fact that at 0° ammonium thiocyanate absorbs ammonia up to 45 per cent. of its weight. A wide-necked bottle about 500 c.c. in capacity is fitted with a stopper carrying an inlet and outlet tube, each of which is provided with a stop-cock. The bottle is filled with the dry salt and is surrounded by ice, and the inlet tube connected with an ammonia generator, when the gas is very rapidly absorbed. After the salt has become saturated, the stop-cocks are closed and the bottle is placed in water and maintained at the ordinary temperature or a little above. The dry gas may then be drawn off as required. It is advisable to recharge the apparatus before the salt commences to crystallise from the liquid in order to guard against the blocking of the inlet tube.

⁴⁸ E. Terres and H. Weiser, *Z. Elektrochem.*, 1921, **27**, 177; *A.*, ii, 448.

⁴⁹ H. W. Foote and S. R. Brinkley, *J. Amer. Chem. Soc.*, 1921, **43**, 1178; *A.*, ii, 448.

By the addition of a solution of antimony trioxide in hydrochloric acid to a solution of sodium thiosulphate and the chloride of an alkali or alkaline-earth metal at about 3° , the stibio-thiosulphates are formed.⁵⁰ The salts may be crystallised at low temperatures or precipitated by the addition of alcohol. The reaction proceeds according to the equation $\text{SbOCl} + 2\text{HCl} + 3\text{K}_2\text{S}_2\text{O}_3 = 3\text{KCl} + \text{H}_2\text{O} + \text{K}_3\text{Sb}(\text{S}_2\text{O}_3)_3$, and the constitution of the salt is represented by $\text{Sb}(\text{S}\cdot\text{SO}_2\cdot\text{OK})_3$. The sodium salt is extremely soluble and has not been prepared in the solid state. The potassium salt forms silk-like, needle-shaped crystals, very similar in appearance to asbestos. The barium salt is white and not very stable. It quickly becomes yellow and finally very deep yellow in colour, owing to decomposition. The potassium salt, on heating, decomposes according to the equation $2\text{K}_3\text{Sb}(\text{S}_2\text{O}_3)_3 = \text{Sb}_2\text{S}_3 + 3\text{K}_2\text{SO}_4 + 3\text{SO}_2 + 3\text{S}$. The aqueous solution, when boiled, decomposes with deposition of the orange-red compound, Sb_2SO_2 .

The corresponding potassium arseno-thiosulphate,⁵¹ $\text{K}_3\text{As}(\text{S}_2\text{O}_3)_3$, has been prepared in an exactly analogous manner. It is a white substance which is not very stable when moist. Its aqueous solution, on boiling, decomposes to give potassium trithionate according to the equation

$(\text{KO}\cdot\text{SO}_2\cdot\text{S})_3\text{As} + \text{As}(\text{S}\cdot\text{SO}_2\cdot\text{OK})_3 = \text{As}_2\text{S}_3 + 3\text{KO}\cdot\text{SO}_2\cdot\text{S}\cdot\text{SO}_2\cdot\text{OK}$, and from this it would seem that trithionic acid has the persulphide formula.

Group VI.

It is known that by the action of ozone on sodium hydroxide and potassium hydroxide orange-coloured products are obtained which are believed to be ozonides or higher oxides.⁵² Attempts have been made to prepare these substances by the action of ozone on solutions of the alkali and alkaline-earth metals in liquid ammonia.⁵³ Although the compounds were precipitated, difficulties were caused by the action of ozone on ammonia. The ozonides, therefore, could not be obtained in a pure state. They are readily decomposed by water and dilute acids with evolution of oxygen and formation of hydrogen peroxide. The ozonides of rubidium and caesium are more stable than the sodium, potassium, calcium, and barium compounds.

It was found that ozone is quantitatively reduced by liquid ammonia, the products being about 98 per cent. of ammonium nitrate and 2 per cent. of nitrite. The first action of the ozone is to

⁵⁰ J. v. Szilágyi, *Z. anorg. Chem.*, 1920, **113**, 69; *A.*, ii, 207.

⁵¹ *Idem*, *ibid.*, 75; *A.*, ii, 199.

⁵² W. Traube, *Ber.*, 1912, **45**, 2201; *A.*, 1912, ii, 844.

⁵³ W. Strecker and H. Thienemann, *ibid.*, 1920, **53**, [B], 2096; *A.*, ii, 44.

produce an orange colour, which may be due to an unstable ozonide. Ozone also reacts with methylamine, dimethylamine, and trimethylamine. In the last case, the reaction is explosive, even at -60° . A 5—10 per cent. solution of trimethylamine in chloroform gives on treatment with ozone trimethylamine oxide, $\text{O}:\text{N}(\text{CH}_3)_3$, which is precipitated as the hydrochloride, the hydrogen chloride being formed by the action of ozone on chloroform.

Very stable colloidal solutions of selenium⁵⁴ may be prepared by the regulated action of concentrated hydrazine hydrate solution on selenium dioxide or grey, crystalline selenium, and subsequent dilution of the solutions with water and purification by dialysis. These solutions vary in colour from intense yellow to blood-red, and when dilute are stable at the boiling point.

When selenium sols produced by the action of sulphur dioxide on solutions of selenious acid at 60° are frozen, the destruction caused by the freezing is greater the more completely the solutions have been purified by dialysis.⁵⁵ Even although the solutions are completely frozen, the greater part of the colloid goes back into solution after melting. If the freezing is repeated many times, or if the solution is kept in the frozen condition too long, the colour by transmitted light becomes less intense and the stability of the sol becomes much less, particularly towards an increase in temperature. The nature of the reducing agent employed in the preparation of the sols and the temperature of preparation have a great influence on the stability toward freezing. Sols prepared by reduction with hydrazine at 60° and dialysed are much more sensitive to freezing than those prepared by reduction with sulphur dioxide at the ordinary temperature. The hydrazine sols coagulated irreversibly on cooling even before solidification occurred. In the case of the sulphur dioxide sols, the concentration of the undialysed sol has a marked influence on the stability towards a reduction of temperature. The more concentrated sols are more readily destroyed by freezing than the more dilute solutions.

Three methods have been given for the preparation of selenium oxychloride.⁵⁶ Selenium in solution in carbon tetrachloride is treated with chlorine. Selenium monochloride is first formed and remains dissolved in the carbon tetrachloride. If any metallic impurities in the selenium are present, these are precipitated as chlorides and may be separated by filtration at this stage. The solution is then saturated with chlorine and selenium tetrachloride is precipitated. The calculated quantity of selenium dioxide is

⁵⁴ A. Gutbier and R. Emslander, *Ber.*, 1921, **54**, [B], 1974; *A.*, ii, 636.

⁵⁵ A. Gutbier and F. Flury, *Kolloid Z.*, 1921, **29**, 161; *A.*, ii, 693.

⁵⁶ V. Lenher, *J. Amer. Chem. Soc.*, 1920, **42**, 2498; *A.*, ii, 109.

added, when selenium oxychloride is formed and the whole passes into solution. The selenium oxychloride may readily be separated from the carbon tetrachloride by fractionation. Since selenium oxychloride readily dissolves selenium, the preparation may very conveniently be carried out by mixing equivalent quantities of selenium and selenium dioxide, adding selenium oxychloride, and treating the mixture with chlorine.

The second method consists in the partial hydrolysis of selenium tetrachloride, which may be carried out with the solid tetrachloride or with the tetrachloride suspended in carbon tetrachloride or selenium oxychloride.

The third method is the dehydration of the compound $\text{SeO}_2 \cdot 2\text{HCl}$, which is an amber-coloured liquid and can be prepared by treating selenium dioxide with dry hydrogen chloride at moderately low temperatures. The liquid is mixed with an excess of phosphoric oxide or calcium chloride, and the oxychloride obtained by distillation. Alternatively, selenium dioxide may be mixed with the dehydrating agent and treated with hydrogen chloride in the cold. On heating the mixture, the selenium oxychloride passes off.

Selenium oxychloride is a nearly colourless liquid with b. p. 176.4° at 726 mm. and m. p. 8.5° .⁵⁷ Amongst many interesting properties of this substance the following may be mentioned. Sulphur, selenium, and tellurium dissolve readily in cold selenium oxychloride, but when the solutions are heated complicated reactions take place. Red phosphorus reacts with selenium oxychloride in the cold with evolution of light and heat, whilst with yellow phosphorus the reaction is explosive. Bromine and iodine give solutions which are very reactive and are coloured reddish-brown and violet respectively. Boron, silicon, and carbon are not attacked in the cold.

Most of the metals are attacked by selenium oxychloride with formation of the chloride of the metal and selenium monochloride, Se_2Cl_2 . There is a remarkable difference in the behaviour of sodium and potassium with the oxychloride. No action takes place with sodium, indeed the oxychloride may be distilled off this metal. Potassium, on the other hand, when brought into contact with selenium oxychloride in the cold, explodes with great violence. Aluminium, zinc, bismuth, and tin are readily attacked, whilst only slow reaction takes place with calcium, copper, magnesium, chromium, lead, nickel, arsenic, cadmium, cobalt, gold, and platinum. Powdered antimony takes fire when introduced into the liquid.

Selenium oxychloride dissolves selenium dioxide to a limited

⁵⁷ V. Lenher, *J. Amer. Chem. Soc.*, 1921, **43**, 29; A., ii, 256.

extent. It also dissolves arsenious oxide, vanadium pentoxide, and molybdenum trioxide, all of which are chemically acted on. The solution of molybdenum trioxide shows a striking photochemical reaction, for on exposure to bright light it becomes blue in a few minutes, the solution regaining its original pale yellow colour within a few hours when kept in a subdued light. Sulphur trioxide dissolves in selenium oxychloride to form a viscous, heavy solution which has powerful solvent properties. It dissolves the oxides of aluminium, chromium, titanium, columbium, molybdenum, vanadium, uranium, and the rare earths; it dissolves the oxide of titanium very slowly and has no action on the oxides of zirconium and tungsten.

The same care is required in handling selenium oxychloride as with any other highly corrosive liquid. Its vapour has no other physiological action than that of the hydrogen chloride produced by its hydrolysis.

Group VII.

Some interesting work has been carried out on the equilibria of hydrofluosilicic acid.⁵⁸ When a solution of hydrofluoric acid was titrated against sodium hydroxide with phenolphthalein as indicator, an apparently considerable excess of alkali could be run in and yet the colour disappeared again after a few seconds. It was found that this was due to the presence of hydrofluosilicic acid, even although the hydrofluoric acid was of A.R. standard.

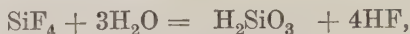
A method of investigation of the proportions in which the two acids are present in the mixture was described by Katz,⁵⁹ and consists in the precipitation of potassium silicofluoride by the addition of potassium chloride solution followed by alcohol. The solution, after filtration, is titrated, and, further, an equal volume of the original solution is titrated, phenolphthalein being used as indicator in each case. The method is rendered inaccurate by the adsorption of some hydrogen fluoride by the colloidal potassium silicofluoride. For the complete neutralisation of hydrofluosilicic acid according to the equation $\text{H}_2\text{SiF}_6 + 6\text{NaOH} = 6\text{NaF} + \text{H}_2\text{SiO}_3 + 3\text{H}_2\text{O}$, an appreciable time is required,⁶⁰ and it has now been found that this is due to the relatively slow dissociation of sodium silicofluoride according to the equation $\text{Na}_2\text{SiF}_6 = 2\text{NaF} + \text{SiF}_4$, it being proved that the reaction is unimolecular. This has enabled a determination to be made of the composition of mixtures

⁵⁸ L. J. Hudlestone and H. Bassett, *T.*, 1921, **119**, 403.

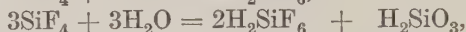
⁵⁹ J. Katz, *Chem. Zeit.*, 1904, **28**, 356, 387; *A.*, 1904, ii, 442.

⁶⁰ C. R. Wagner and W. H. Ross, *J. Ind. Eng. Chem.*, 1917, **9**, 1116.

of the two acids. When silicon tetrafluoride is passed into water, the reaction may be expressed by the equations :—



and



by addition.

The reactions must be reversible, since hydrofluosilicic acid is formed equally by the action of silicon tetrafluoride on water and of hydrofluoric acid on silica, and also hydrofluosilicic acid with sufficient alkali yields, ultimately, sodium fluoride and silicic acid. Therefore all four substances must be present in finite, even although possibly very small, concentration in these solutions. Further, these solutions, filtered from the precipitated silicic acid, on titration by Katz's method, react like pure hydrofluosilicic acid, so that the free hydrofluoric acid cannot be in excess of that required to combine with the free silicon tetrachloride and silicic acid to form hydrofluosilicic acid.

A determination of the amounts present in a solution which in total acidity was 0.05*N* showed the following— SiF_4 0.0005 mol. per litre, H_2SiF_6 0.0045 mol. per litre, and HF 0.021 mol. per litre. It was also proved that the silicic acid must be present in true solution, since its active mass varies with dilution in the ordinary way.

When a mixture of potassium perchlorate (3 parts) and chlorosulphonic acid (5 parts) is gradually heated to 70—75° in a vacuum, a mixture of chlorine heptoxide and pyrosulphuryl chloride passes over.⁶¹ Pale yellow chlorine heptoxide (98—99 per cent.) is prepared by the distillation of the product in a vacuum, but traces of sulphur compounds are obstinately retained even after repeated distillation. The process is almost free from danger.

Chlorine heptoxide in a higher state of purity can be obtained by the very cautious addition of phosphoric oxide to strongly-cooled perchloric acid (70 per cent.) in such a manner that the heptoxide can ultimately be distilled, but local overheating cannot be avoided and the yields are poor. Pure solutions of chlorine heptoxide in carbon tetrachloride may be prepared by this method. Considerable amounts of phosphoric oxide are suspended in carbon tetrachloride, the mixture is cooled to 0° and violently stirred, while perchloric acid is added drop by drop. The mixture is warmed and filtered and yields a solution containing about 2.5 per cent. of chlorine heptoxide. If this solution is distilled as far as possible at 0° in a water-pump vacuum, a residue remains which contains about 1/3 of the original carbon tetrachloride and 80 per cent. of the heptoxide.

⁶¹ F. Meyer and H. G. Kessler, *Ber.*, 1921, **54**, [B], 566; *A.*, ii, 326.

A colloidal solution of manganese dioxide may conveniently be prepared by the reduction of dilute solutions of potassium permanganate by means of ammonia.⁶² A *N*/20-solution of potassium permanganate is heated to the boiling point and, while stirring, concentrated ammonia solution is added at the rate of one drop every three or four minutes. At no time should anything but the faintest smell of ammonia be perceptible. The solution gradually turns wine-red and finally becomes coffee-brown. To test if all the permanganate has been reduced, a little of the colloidal solution may be coagulated by the addition of sodium chloride to show the presence of any violet colour which might have been masked by the colloid. The product only contains potassium hydroxide as an impurity, and as this substance has no action on the colloid, it may be left in the solution. This eliminates the necessity of removing the electrolyte by dialysis, especially since the colloid is coagulated by filter paper or parchment. The colloid at all concentrations catalyses the decomposition of hydrogen peroxide. The concentrated solutions are coagulated during the reaction, whilst dilute solutions are unaffected. The colloid is perfectly stable in the presence of alcohol of all concentrations.

Group VIII.

The formation of sodium ferrite and ferrate by electrolysis of sodium hydroxide solution with iron anodes has been investigated,⁶³ and it is found that these salts only are formed, since the iron passes into solution only in the bivalent or sexavalent condition. Sodium ferrite may also be obtained by cathodic reduction of a solution of sodium ferrate. Measurements of the equilibrium potential of iron against a sodium ferrite solution and of platinum against mixtures of ferrite and ferrate show that the ferrite solution is more complex than is represented by the simple formula Na_2FeO_2 .

Commercial platinum may be freed from the impurities it usually contains by repeated precipitation as ammonium platinichloride.⁶⁴ It was found that a sample of platinum containing palladium, rhodium, and iridium, as well as considerable amounts of tin, iron, and other metals, can be obtained in the pure state by four such precipitations. Each precipitate of ammonium platinichloride is drained on a Buchner funnel, stirred with a considerable volume of 15–20 per cent. ammonium chloride solution, and again drained, this process being repeated two or three times. The washed pre-

⁶² E. J. Guy, *J. Physical Chem.*, 1921, **25**, 415; *A.*, ii, 642.

⁶³ G. Grube and H. Gmelin, *Z. Elektrochem.*, 1920, **26**, 459; *A.*, ii, 49.

⁶⁴ E. Wichers, *J. Amer. Chem. Soc.*, 1921, **43**, 1268; *A.*, ii, 648.

precipitate is dried, ignited to platinum sponge in an electrically heated muffle, and dissolved in aqua regia. The solution is evaporated several times with hydrochloric acid to remove nitric acid and precipitated with ammonium chloride. The amount of platinum left in the mother-liquor from the precipitate is usually not more than 1 per cent. of that in the precipitate. The final precipitate is ignited to sponge in a porcelain dish over a gas flame in a current of hydrogen.

In the Reports for the last two years reference was made to work on the occlusive power of platinum and palladium for hydrogen, and brief mention may be made of some further investigations. In the first place, it has been confirmed that the amount of hydrogen occluded by palladium is determined by the relative amounts present of the two forms of the metal, the amorphous and the crystalline.⁶⁵ In all probability this explains the divergent results obtained by Hemptinne⁶⁶ and by Paal and Amberger,⁶⁷ since the occlusive power of the crystalline variety is very much reduced at low temperatures.

In last year's Report the reporter criticised Dr. Maxted's interpretation of the results he obtained on the poisoning of palladium by hydrogen sulphide, and suggested that the adsorption of hydrogen consists of two separate processes, first, the occlusion of hydrogen as atoms, followed by a secondary effect of condensation as molecules. Dr. Maxted has now brought forward evidence which strongly supports this view, and, moreover, brings the results more into agreement with the modern views of catalytic activation by metals.⁶⁸ This is well shown by the results obtained on the poisoning of palladium by lead, in which for a known lead content both the occlusive power for hydrogen and the catalytic activity of the product were measured. The catalytic activity is a linear function of the lead content up to a stage in which the greater part of the activity has been suppressed. A point of inflection occurs at this stage, below which the decrease of activity caused by further addition of lead falls off far less steeply. The occlusive power for hydrogen is also a linear function of the lead content, but the slope of the two lines is very different. Thus, a ratio of 0.17 gram-atom of lead to 1 gram-atom of palladium is required to reduce the occlusive power to one-half, whilst in order to reduce the catalytic activity to one-half, only about 0.02 gram-atom of lead to each

⁶⁵ J. B. Firth, *T.*, 1921, **119**, 1120.

⁶⁶ A. de Hemptinne, *Bull. Acad. roy. Belg.*, 1898, [iii], **36**, 155; *A.*, 1899, ii, 228.

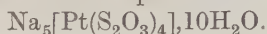
⁶⁷ C. Paal and C. Amberger, *Ber.*, 1905, **28**, 1394; *A.*, 1905, ii, 397.

⁶⁸ E. B. Maxted, *T.*, 1920, **117**, 1501; 1921, **119**, 1280.

gram-atom of palladium is necessary. It is probable therefore that, whilst the occlusion is not confined to the surface only of the palladium, catalysis is mainly a surface phenomenon. This view is strengthened by the fact that the slope of the poisoning line for catalytic activity varies with the fineness of division of the catalyst.

It is evident from these observations that, as suggested, there are two processes, namely, the adsorption and activation of the hydrogen on the surface of the catalyst, and the condensation of more hydrogen as molecules within the capillaries. Apart from the bearing of this on Dr. Maxted's previous work, it has considerable importance from the energy side, since energy must be given to the hydrogen molecules in order to activate them. This energy must be supplied by the palladium, and it is not possible to believe that this action can extend beyond a molecular layer of hydrogen distributed over the surface of the metal. In this connexion recent experimental work tends more and more to show that in all similar cases of heterogeneous catalysis the thickness of the activated layer is of molecular dimensions.

By the reduction of sodium platinichloride with an excess of sodium hyposulphite a dark reddish-brown solution is obtained which, on slow evaporation, deposits a precipitate which is a complex mixture of sodium platinosulphite compounds with $\text{Na}_2\text{Pt}_4\text{S}_6$.⁶⁹ After filtration, the solution first deposits crystals of sodium platini-sulphite, $\text{Na}_4[\text{Pt}(\text{SO}_3)_3(\text{OH})_2] \cdot \text{H}_2\text{O}$, and then, on further evaporation, bright yellow crystals of sodium platinothiosulphate,



By reduction of iridium tetrachloride in neutral solution sodium iridosulphite, $\text{Na}_6[\text{Ir}(\text{SO}_3)_4] \cdot 10\text{H}_2\text{O}$, was obtained in bright yellow crystals. The following salts were also prepared,

$\text{Na}_6[\text{Rh}_4(\text{SO}_3)_7] \cdot 12\text{H}_2\text{O}$; $\text{Na}_6[\text{Os}_4(\text{SO}_3)_7] \cdot 24\text{H}_2\text{O}$, and $\text{Na}_3\text{H}_3[\text{Ru}(\text{SO}_3)_4]$.

E. C. C. BALY.

⁶⁹ G. Sailer, *Z. anorg. Chem.*, 1921, **116**, 209; *A.*, ii, 513.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

THE usual arrangement of this division of the Annual Reports has been followed, except that the section dealing with optical activity has been omitted this year as only a few papers on the subject have appeared.

Hydrocarbons.

The problem of converting natural paraffin into a mixture of fatty acids is still receiving attention, although apparently very little progress has been made. Schaarschmidt and Thiele¹ chlorinate paraffin at 160° and then remove hydrogen chloride either by treatment with alkali or by simply heating at about 300°; the resulting mixture of olefines is then oxidised, preferably by ozone, and under the best conditions a yield of about 60 per cent. of the higher fatty acids is obtained. No better results were obtained by Gränacher,² who oxidised heated paraffin wax by a current of air containing 2 per cent. of nitrogen peroxide. At 150°, the process requires about four days. When *n*-undecane is treated in the same manner, nonoic is the highest acid formed, and this only in small quantity. The method is therefore unsuitable for the degradation of hydrocarbons, but shows that the higher paraffins in nature must consist only to a small extent of normal hydrocarbons.

The combination of acetylene with water in the presence of various catalysts to form acetaldehyde has again been investigated, mainly because of the difficulty of regenerating the catalysts; this can be done, when oxides such as molybdic acid are used, by a current of air at a high temperature³ or by the periodic addition of ferric oxide to a heated solution of mercuric sulphate.⁴ In this connexion, the discovery by W. J. Jenkins⁵ of a new compound of acetylene and mercuric chloride, $\text{HgCl}_2 \cdot 2\text{C}_2\text{H}_2$, which contains double the amount of acetylene to that in the well-known compound,

¹ *Ber.*, 1920, **53**, [B], 2128; *A.*, i, 1.

² *Helv. Chim. Acta*, 1920, **3**, 721; *A.*, i, 2.

³ D. R.-P. 334357; *A.*, i, 542.

⁴ *Brit. Pat.* 140784; *A.*, i, 706.

⁵ *T.*, 1921, **119**, 747.

may be of some practical interest. Kindler ⁶ has observed that gold is quantitatively precipitated from dilute solutions of the auric haloids by acetylene, which is thereby converted into glyoxal.

Alcohols and Derivatives.

Very little research has been published on alcohols during the year, but a few new methods of preparation are of interest.

Methyl alcohol ⁷ is readily purified from acetone by taking advantage of the fact that methyl alcohol and chloroform form a binary mixture boiling at 53° at atmospheric pressure. In practice, 1 part of the crude alcohol is mixed with 7.5 parts of chloroform, the mixture distilled, and then from the fraction boiling at about 53° the methyl alcohol is extracted by water, the aqueous alcohol being rectified in the usual manner.

Acetaldehyde ⁸ can be reduced in an economical manner if led into the cathode chamber of an electrolytic cell charged with a suitable acid medium in such a manner that the concentration of the acetaldehyde in the solution is maintained low. When this does not exceed about 5 per cent. the yield of alcohol is good and the current efficiency high.

The preparation of primary alcohols by the action of Grignard's reagents on trioxymethylene is rendered very tedious by its sparing solubility in ether and its very gradual depolymerisation. The usual small yields are much improved ⁹ and the time required is much shortened if the vapours from well-dried boiling trioxymethylene are led into a well-stirred Grignard reagent. The yield of the alcohols, $R \cdot CH_2 \cdot OH$, is reduced when R is small (particularly when $R = C_2H_5$), owing to the formation of considerable quantities of the methylene ethers, $CH_2(OR)_2$.

Secondary butyl alcohol is very easily prepared from the butylene formed by the catalytic dehydration of *n*-butanol. The liquefied β -butylene ¹⁰ is mixed with 75 per cent. sulphuric, with phosphoric or with benzenesulphonic acid, either at the ordinary temperature under increased pressure or at -10° under atmospheric pressure. When absorption of the hydrocarbon is complete, the liquid is diluted with water and the secondary alcohol distilled over with a current of steam.

Many of the preparations carried out by modern methods of

⁶ *Ber.*, 1921, **54**, [B], 647; *A.*, i, 396.

⁷ A. Lanzenberg and J. Duclaux, *Bull. Soc. chim.*, 1921, [iv], 29, 135; *A.*, i, 298.

⁸ Chem. Fabrik Greisheim Elektron, D. R.-P. 328342; *A.*, i, 155.

⁹ K. Ziegler, *Ber.*, 1921, **54**, [B], 737; *A.*, i, 394.

¹⁰ C. Weizmann and D. A. Legg, *Brit. Pat.* 161591; *A.*, i, 493.

catalysis at high temperatures are unsatisfactory owing to contamination with small amounts of impurities formed by isomeric change under the influence of the catalyst. This phenomenon is well illustrated by a quantitative study of the products of the dehydrogenation of the mixture of amyl alcohols produced by fermentation. Using aluminium silicate heated at 350° as the catalyst, Senderens¹¹ has shown that the relative proportion of the three hydrocarbons, β -methyl- Δ^{β} -butene, β -methyl- Δ^{α} -butene, and γ -methyl- Δ^{α} -butene, the last two of which may be assumed to be formed direct from the β -methylbutan- α -ol, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$, and from the isobutylcarbinol respectively, varies considerably with the age of the catalyst. In the fermentation alcohol there is generally about 87 per cent. of isobutylcarbinol and 13 per cent. of the optically active constituent, but the proportion of γ -methyl- Δ^{α} -butene is always very much less than that of the β -methyl isomeride. When the catalyst is new and active, nearly four-fifths of the product consists of β -methyl- Δ^{β} -butene obviously formed by isomeric change from β -methyl- Δ^{α} -butene under the influence of the catalyst, since, when this ages, the proportion of these two hydrocarbons in the product becomes nearly equal, whilst that of the γ -methyl- Δ^{α} -butene, which is only one-thirtieth with the fresh catalyst, amounts to one-fifth of the product.

The proportion of the various isomerides may, moreover, depend on the pressure, for Moureu and Mignonac¹² have shown that this affects the dehydrogenation of alcohols when this is carried out by contact with oxygen and finely divided silver at 230 — 300° .

The reaction between alcohols and hydrogen sulphide to form mercaptans¹³ is brought about by specially prepared thorium oxide at 380° . The catalyst needs to be formed from the nitrate by decomposition of this in a current of air at 270° , and thus differs from the ordinary thoria commonly used as a catalyst in other reactions. The yields amount to 40 to 50 per cent. when the vapour of the alcohol and the hydrogen sulphide are passed over the catalyst at the rate of 1 gram-molecule per hour. The mercaptans give mixtures of constant boiling point with the corresponding alcohols and are best purified by means of their lead salts.

Acids and their Derivatives.

It is well known that the acetylating action of acetic anhydride is often increased by the addition to it of traces of concentrated

¹¹ *Compt. rend.*, 1920, **171**, 916; *A.*, i, 4.

¹² *Ibid.*, 652; *A.*, 1920, i, 805.

¹³ R. L. Kramer and E. E. Reid, *J. Amer. Chem. Soc.*, 1921, **43**, 880; *A.*, i, 389.

sulphuric acid. This is probably due to the formation of small amounts of acetylsulphuric acid, $\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$, the preparation and properties of which have been described by van Peski.¹⁴ It is formed when sulphur trioxide acts on acetic acid at 0° , and reacts with sodium acetate to form sodium acetylsulphate. This salt, when heated, decomposes, giving sodium pyrosulphate and acetic anhydride, but when heated with acetic acid gives acetic anhydride and sodium hydrogen sulphate, a reaction which is reversible. When heated at 70° , acetylsulphuric acid is converted into sulpho-acetic acid, which is readily acetylated by acetylsulphuric acid, forming acetylsulphoacetic acid; the latter readily condenses to

form disulpho-dehydroacetic acid,
$$\begin{array}{c} \text{CH}_3\cdot\text{CO} \\ \text{SO}_3\text{H} \end{array} > \text{C} < \begin{array}{c} \text{CO}\cdot\text{O}\cdot\text{CMe} \\ \text{CO}-\text{C}\cdot\text{SO}_3\text{H} \end{array}$$

Acetylsulphuric acid is a very vigorous acetylating agent, acetylating, for example, tribromophenol with ease; in some cases, however, it acts as a sulphonating agent, converting benzene, for example, into benzenesulphonic acid.

Acetylene will combine with acetic acid to form ethylidene diacetate quantitatively under certain conditions in the presence of a variety of catalysts. The best of these appear to be methylene sulphate at about 50° , methyl sulphate¹⁵ at about 75° , or mercury naphthalene- β -sulphonate¹⁶ at a temperature of about 50° .

Zirconium oxide¹⁷ must be added to the list of substances which are capable of bringing about the condensation of the vapours of acids and alcohols to form esters. This catalyst works best at a temperature of 270 – 290° , whilst the yield of ester depends on the weight of oxide used, the velocity of the flow of the vapours, and the proportion of acid and alcohol used.

There have been many observations of interaction between esters and alcohols in the presence of catalysts, leading to the formation of new esters. Attention was directed by Fischer¹⁸ to the fact that glycerol α -monobenzoate is moderately rapidly converted in ethereal solution in the presence of potassium carbonate into a mixture of glycerol and a dibenzoate. The process is more conveniently followed with the benzoyl derivatives of ethylene glycol in chloroform solution, whereby it is shown that the change is balanced and attains an equilibrium in the presence of the glycol and the mono- and dibenzoates. Similarly, glycerol monoacetate is largely transformed

¹⁴ *Rec. trav. chim.*, 1921, **40**, 103; *A.*, i, 302.

¹⁵ D. R.-P. 322746; *A.*, 1920, i, 810.

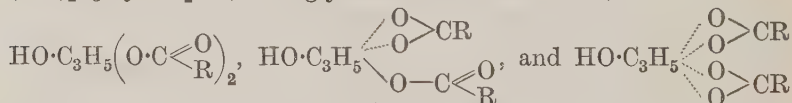
¹⁶ *Ibid.*, 334554; *A.*, i, 535.

¹⁷ A. Mailhe and F. de Godon, *Bull. Soc. chim.*, 1921, [iv], **29**, 101; *A.*, i, 219.

¹⁸ E. Fischer, E. Pfähler, and F. Brauns, *Ber.*, 1920, **53**, [B], 1634; *A.*, 1920, i, 840.

into diacetin and glycerol. The action of the potassium carbonate appears to be definitely catalytic, since very small amounts of it suffice to accelerate the change. The phenomena recorded in this paper are very similar to those first observed by Purdie,¹⁹ who found that an exchange of alkyl radicles readily took place between simple esters and alcohols in the presence of a small amount of sodium alkyloxide. Grün²⁰ has now shown that this interchange of alkyl groups between fats and alcohols can take place under certain conditions even in the absence of catalysts.

Such phenomena explain to some extent the gradual change in melting point observed by Grün to take place when diacyl derivatives of glycerol are preserved and also of the so-called "ageing" of the natural fats. This, however, is not a complete explanation of all the facts, as some of the triglycerides are known in more than one form, as, for example, tristearin, which exists in two forms, m. p. 55° and 71° respectively. Grün prefers to regard these as examples of co-ordination isomerism, in which most of the esters (fats) may be regarded as an equilibrium mixture of the forms $R \cdot C \begin{smallmatrix} O \\ \diagup \\ \diagdown \end{smallmatrix} OR'$ and $R \cdot C \begin{smallmatrix} O \\ \diagdown \\ \diagup \end{smallmatrix} R'$. According to the author's views, then, a monoglyceride can exist in two forms, $(OH)_2C_3H_5 \cdot O \cdot C \begin{smallmatrix} O \\ \diagup \\ \diagdown \end{smallmatrix} R$ and $(OH)_2C_3H_5 \cdots O_2CR$, a diglyceride in three forms,



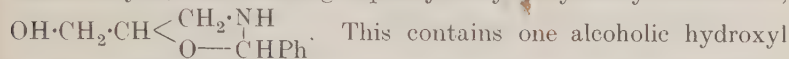
whilst a triglyceride formed from a single acid can exist in four forms, namely, the ordinary ester and pure co-ordination varieties and two mixed types. Thus the co-ordination form of a triglyceride formed from a single acid only can pass into the true ester form, but from the co-ordination form of a mixed triglyceride, a mono- or a di-glyceride, all the structural isomerides can, in addition, be produced. This hypothesis, although somewhat intangible, does serve to correlate the numerous and otherwise confusing facts which are recorded in the author's papers, and is very similar to those put forward by other investigators to explain the abnormal physical properties of some esters.

The phenomena described in the preceding paragraphs render the synthesis of pure glycerides a matter of some considerable difficulty. For this reason, a method for the synthesis of optically active $\alpha\beta$ -

¹⁹ T. Purdie, *T.*, 1887, **53**, 391.

²⁰ A. Grün, F. Wittka, and J. Scholze, *Ber.*, 1921, **54**, [B], 273, 290; *A.*, i, 220, 222.

diglycerides and unsymmetrical triglycerides in which the position of the respective acyl groups is tolerably certain is very welcome. Such a synthesis which, although somewhat complex, seems to avoid the possibility of the interchange of acyl groups, is described by M. Bergman and his co-workers.²¹ The starting point is γ -amino- $\alpha\beta$ -propylene glycol, which is readily obtained by the action of ammonia on glycide. The aminoglycol is first of all condensed with benzaldehyde, thus forming 2-phenyl-5-hydroxymethyl-oxazolidine,



group, which can be acylated. The ring in the resulting acylated compound is readily opened up with the elimination of benzaldehyde, giving compounds of the formula $\text{OA}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NHA}$. These can be treated with another acylating agent, giving compounds of the type $\text{OA}\cdot\text{CH}_2\cdot\text{CH}(\text{OB})\cdot\text{CH}_2\cdot\text{NHA}$. Mild treatment with phosphorus pentachloride and water converts these into compounds of the type $\text{OA}\cdot\text{CH}_2\cdot\text{CH}(\text{OB})\cdot\text{CH}_2\cdot\text{NH}_2$, which can be resolved into their optically active components. By treatment with nitrous acid, there are obtained $\alpha\beta$ -diglycerides, $\text{OA}\cdot\text{CH}_2\cdot\text{CH}(\text{OB})\cdot\text{CH}_2\cdot\text{OH}$, which can be converted into unsymmetrical triglycerides. The presence of two asymmetric carbon atoms in the oxazolidine does not interfere with these syntheses, as one disappears on removal of the benzaldehyde when the ring is ruptured.

So far, the syntheses have been carried out only with benzoyl and nitro- and chloro-substituted benzoyl groups as acylating agents. The resolution of γ -aminopropylene $\alpha\beta$ -dibenzoate was effected by crystallisation of its quinate, and after treatment with nitrous acid gave the oily *l*-glycerol $\alpha\beta$ -dibenzoate. This was further treated with *p*-nitrobenzoyl chloride, giving *l*-glyceryl $\alpha\beta$ -dibenzoate γ -*p*-nitrobenzoate with m. p. 114° and with $[\alpha]_D - 1.9^\circ$ in *s*-tetrachloroethane. This compound is claimed by the authors to be the first example of the synthesis of a homogeneous, optically active triglyceride. It may be pointed out, however, that the homogeneous character of their preparation is not definitely proved, whilst the low rotation may be caused by racemisation during its production.

M. Tsujimoto²² has observed that the lithium salts of the more highly unsaturated acids derived from fish oils are readily soluble in acetone containing 5 per cent. of water, and since those of the saturated or slightly unsaturated acids are insoluble in this solvent a separation can be effected and gives amounts of highly unsaturated acids which are considerably higher than those calculated from the yields of the polybromides.

²¹ *Ber.*, 1921, **54**, [B], 936; *A.*, i, 444.

²² *J. Chem. Ind. Japan*, 1920, **23**, 1007; *A.*, i, 78.

For the synthesis of the basic derivatives of cocaine, succinyl-diacetic acid is a convenient starting point. A satisfactory preparation of this acid has been described by Willstätter and Pfannenstiel,²³ who have obtained the dipotassium derivative of the enolic form of ethyl hydrogen acetonedicarboxylate, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{OK})\cdot\text{CH}\cdot\text{CO}_2\text{K}$. A solution of this compound, after neutralisation by oxalic acid of the enolic potassium, is readily converted by electrolysis into the diethyl ester of the required acid, $\text{C}_2\text{H}_4(\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, which shows the properties of an enol and exhibits the reactions of a β -ketonic ester. The acid and its esters readily condense with amines to give pyrrole derivatives of the type $\text{NMe} < \begin{matrix} \text{C}(\text{CH}_2\cdot\text{CO}_2\text{Et})\cdot\text{CH} \\ \text{C}(\text{CH}_2\cdot\text{CO}_2\text{Et})\cdot\text{CH} \end{matrix}$.

In last year's Report, the successful separation was described of the keto-form of ethyl acetoacetate by K. Meyer and co-workers, who fractionated the equilibrium mixture in specially cleaned distillation flasks of quartz under a pressure of 2 mm. The isolation of the pure enol form is now described.²⁴ For this purpose, the equilibrium ester is distilled from a Jena glass flask in the presence of a trace of phthalic acid. The distillate, which is collected in a quartz receiver, contains nearly 90 per cent. of the enol and is immediately refractionated from a silica apparatus, the first fraction being composed of the pure enol. Similar results have been obtained by distillation of acetylacetone, which, however, appears to be far more sensitive than ethyl acetoacetate to the influence of catalysts.

Ingold²⁵ has investigated the mechanism underlying the reaction of ethyl cyanoacetate with tautomeric compounds and shown that in the great majority of cases the first stage is the addition of the cyano-ester to the double bond. This in all probability is the reason why the polyacetic acids of methane such as the triacetic acid, $\text{CH}(\text{CH}_2\cdot\text{CO}_2\text{H})_3$, carboxytriacetic acid, $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_2\cdot\text{CO}_2\text{H})_3$, and the tetra-acetic acid, $\text{C}(\text{CH}_2\cdot\text{CO}_2\text{H})_4$, are all difficult to prepare, since the corresponding unsaturated acids, $\text{CO}_2\text{H}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\text{CO}_2\text{H}\cdot\text{CH}:\text{C}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and $\text{CO}_2\text{H}\cdot\text{CH}:\text{C}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, are all substances of the glutaconic acid type with a mobile hydrogen atom—a series of compounds which have been shown by J. F. Thorpe and his co-workers to be exceedingly unreactive and not unsaturated in the ordinary sense of the term. Methanetriacetic acid,²⁶ however, can be prepared readily by the condensation of ethyl sodiocyanoacetate with diethyl β -hydroxyglutarate and subsequent hydrolysis of the product. Further investigation²⁷ of

²³ *Annalen*, 1921, **422**, 1; *A.*, i, 91.

²⁴ K. H. Meyer and H. Hopff, *Ber.*, 1921, **54**, [B], 579; *A.*, i, 391.

²⁵ C. K. Ingold, *T.*, 1921, **119**, 329.

²⁶ *Idem*, *ibid.*, 346.

²⁷ C. K. Ingold and E. A. Perren, *ibid.*, 1582.

the condensation of highly substituted glutaconic esters and ethyl cyanoacetate shows that in derivatives of methanetriacetic acid substituents in more than one of the acetic acid chains produce a condition of instability.

Constitution of Grignard's Magnesium Compounds.

The various formulæ, $\begin{smallmatrix} \text{Et} \\ \text{Et} \end{smallmatrix} > \text{O} < \begin{smallmatrix} \text{MgAlk} \\ \text{Hal} \end{smallmatrix}$, $\begin{smallmatrix} \text{Et} \\ \text{Et} \end{smallmatrix} > \text{O} < \begin{smallmatrix} \text{Alk} \\ \text{MgHal} \end{smallmatrix}$, and $\begin{smallmatrix} \text{Et} \\ \text{Et} \end{smallmatrix} > \text{O} < \begin{smallmatrix} \text{MgAlk} \\ \text{Hal:OEt}_2 \end{smallmatrix}$, which have from time to time been assigned to Grignard's reagents must be regarded as unsatisfactory, since they fail to account for the full reactivity of the substances. Meisenheimer and Caspar²⁸ therefore propose to regard them as complex compounds of magnesium in which the central atom has the co-ordination number 4, thus: $\begin{smallmatrix} \text{Et}_2\text{O} \\ \text{Et}_2\text{O} \end{smallmatrix} > \text{Mg} < \begin{smallmatrix} \text{Alk} \\ \text{Hal} \end{smallmatrix}$. In this formula the alkyl group and halogen atom are united to the magnesium by main valencies, the ether molecules by subsidiary valencies. When brought into contact with acetone, etc., the latter, by virtue of its greater reaction energy, displaces a molecule of ether, yielding the substance $\begin{smallmatrix} \text{Me}_2\text{CO} \\ \text{Et}_2\text{O} \end{smallmatrix} > \text{Mg} < \begin{smallmatrix} \text{Alk} \\ \text{Hal} \end{smallmatrix}$. It is suggested that re-arrangement of the bonds within the complex then occurs by which the subsidiary bond between the magnesium and the carbonyl oxygen becomes a chief bond; the alkyl group which has thus become detached from the magnesium atom attaches itself to the chief bond of the carbonyl carbon atom which has simultaneously become free, and the vacant co-ordination position of the magnesium atom is taken by a molecule of ether, thus: $\begin{smallmatrix} \text{Me}_2\text{CAlk}\cdot\text{O} \\ \text{Et}_2\text{O} \end{smallmatrix} > \text{Mg} < \begin{smallmatrix} \text{OEt}_2 \\ \text{Hal} \end{smallmatrix}$. This conception is in complete harmony with the observation of Ahrens and Stapler^{28a} that magnesium bromide and iodide form dietherates from which one molecule of ether can be displaced readily by a molecule of aldehyde, ketone, or amine. It also explains the peculiar behaviour of allyl haloids towards magnesium; as the final product of these reactions, a crystalline mass is obtained which consists entirely of the magnesium haloid dietherate, the allyl radicle being quantitatively contained in the ethereal solution in the form of diallyl. The course of the reaction is explained as follows: The primary reaction consists in the formation of a normal Grignard compound, $\begin{smallmatrix} \text{Et}_2\text{O} \\ \text{Et}_2\text{O} \end{smallmatrix} > \text{Mg} < \begin{smallmatrix} \text{C}_3\text{H}_5 \\ \text{Br} \end{smallmatrix}$, from which a molecule of ether is immediately displaced by a further molecule of allyl bromide,

²⁸ *Ber.*, 1921, **54**, [B], 1655; *A.*, i, 654.

^{28a} *A.*, 1905, i, 868.

$\text{Et}_2\text{O} \begin{array}{c} \nearrow \\ \searrow \end{array} \text{Mg} \begin{array}{c} \nwarrow \\ \swarrow \end{array} \text{C}_3\text{H}_5\text{Br}$. In this complex, the allyl residue of the alkyl haloid is only loosely attached by reason of the union of the bromine atom to the magnesium, which may be thus expressed : $\text{C}_3\text{H}_5 \left[\text{Et}_2\text{O} \begin{array}{c} \nearrow \\ \searrow \end{array} \text{Mg} \begin{array}{c} \nwarrow \\ \swarrow \end{array} \text{C}_3\text{H}_5\text{Br} \right]$. As a consequence, when two such molecules come within range of one another, the allyl residue is readily detached, yielding diallyl. Simultaneously, a change in bonds occurs by which the second bromine atom becomes attached by a main valency to the magnesium atom and the diallyl group by a subsidiary valency. A hydrocarbon such as diallyl has, however, but little free valency, and is therefore readily displaced by the ether, thus giving a magnesium haloid dietherate. The peculiar property of allyl haloids is due to the reactivity of the halogen atom in these compounds and the relatively large amount of the available valency of the halogen atom. It is to be expected further that allyl bromide would have the same power of displacing ether from any similarly constituted Grignard compound. This is shown to be the case, since allyl bromide is found to react with ethereal solutions of magnesium methyl, ethyl, or phenyl bromide to give the magnesium haloid dietherate, and butene, pentene, and allylbenzene respectively.

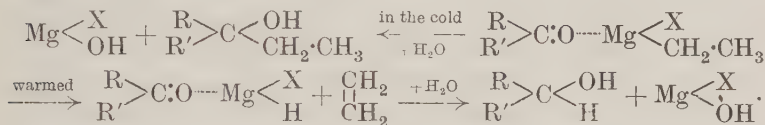
The catalytic activity of ether and tertiary amines in promoting the action between magnesium and alkyl haloids cannot be explained satisfactorily by the assumption of the formation of oxonium salts of the type $\begin{array}{c} \text{Et} \\ \text{Et} \end{array} \text{O} \begin{array}{c} \nearrow \\ \searrow \end{array} \text{Me} \begin{array}{c} \nwarrow \\ \swarrow \end{array} \text{I}$, since in this case a mixture of magnesium methyl and ethyl iodides must result. This difficulty is overcome by considering that the action between ether or base and alkyl haloid proceeds only to the subsidiary valency stage, $\begin{array}{c} \text{Et} \\ \text{Et} \end{array} \text{O} \cdots \text{MeI}$, $\text{Alk}_3\text{N} \cdots \text{PhI}$, which accounts thus for the unusual mobility of the halogen atom.

The reducing action of the Grignard reagent under some conditions is assumed by K. Hess and H. Rheinboldt ²⁹ to be due to magnesium hydrogen haloid. These authors also represent these reagents by co-ordination formulæ. They show that, under the conditions customary in the preparation of Grignard's reagents, magnesium does not react with gaseous hydrogen chloride in the presence of ether or benzene. Liquid hydriodic acid does not attack magnesium, whereas in the presence of dry ether a reaction occurs readily which, however, is due to the ready conversion of ether into ethyl iodide by hydrogen iodide. To avoid complications of this type, the "individual" Grignard compounds were used, when it was found that

²⁹ *Ber.*, 1921, **54**, [B], 2043; *A.*, i, 777.

magnesium ethyl iodide does not react with gaseous or liquid hydrogen iodide, alone or in the presence of benzene, whereas it is decomposed completely by hydrogen chloride with the liberation of ethane. Attempts to demonstrate the unaltered nature of the magnesium ethyl iodide after treatment with hydrogen iodide by bringing it into reaction with benzaldehyde led to the rather surprising isolation of benzyl alcohol instead of the expected phenylethylcarbinol. A similar result was observed with untreated magnesium ethyl iodide in warm benzene and, but to a less extent, in warm ether, whereas phenylethylcarbinol was exclusively obtained in ethereal solution at the atmospheric temperature.

According to these authors, the Grignard compounds can be represented most accurately by co-ordination formulæ, as, for example, $RR'C:O \cdots Mg \begin{smallmatrix} Br \\ < \\ CH_2 \cdot CH_3 \end{smallmatrix}$, and the reductions then occur in accordance with the scheme :



Since it is shown that the subsidiary reaction may be made into the main change by increasing the temperature, it is possible that a method is opened out for the reduction of substances containing the ketonic group and other reducible groups (for example, ethylenic linkings) which are not changed by reduction of the ketonic group. In any case, it is demonstrated that the avoidance of subsidiary reactions in the case of the aliphatic alkyl haloids (except the methyl compounds) can only be secured by the avoidance of elevated temperature, except under perfectly definite conditions.

Catalytic Hydrogenation and Dehydrogenation.

During the last three years much attention has been devoted to finding a satisfactory explanation of the phenomena observed during the catalytic hydrogenation of unsaturated compounds, the activation of the catalysts, and the catalytic dehydrogenation of alcohols.

It is still an open question whether oxygen is necessary for the activation of hydrogenating catalysts, and most of the work recently published bears on this point.

In a series of papers by E. F. Armstrong and T. P. Hilditch,³⁰ the linear nature of the reaction-time curve, at least in the earlier

³⁰ *Proc. Roy. Soc.*, 1919, [A], **96**, 137, 322; *A.*, 1919, ii, 403; 1920, ii, 102; *ibid.*, 1920, [A], **97**, 259; **98**, 27; *A.*, 1920, ii, 422, 608; *ibid.*, 1921, [A], **99**, 490; *A.*, ii, 582 *et seq.*

stages of the reaction, for catalysis at solid surfaces is demonstrated and shown to compare with hydrolysis brought about by means of enzymes. These investigators conclude that unstable complexes of catalyst and unsaturated compound are formed which break down on addition of hydrogen to saturated compound and regenerated catalyst. By this means, they explain the fact that hydrogenation and dehydrogenation may proceed simultaneously, even at the optimum temperature for the former process. They have succeeded, by using the reacting compounds in the liquid state, in hydrogenating an unsaturated compound at the expense of a saturated compound, which thereby undergoes reduction. With reduced nickel as the catalyst, a mixture of *cyclohexanol* and methyl cinnamate at 180° gave a certain amount of *cyclohexanone* and methyl β -phenylpropionate; whilst a mixture of ethyl stearate and methyl cinnamate at 230° produced a small quantity of methyl β -phenylpropionate together with some ethyl oleate, although the amount of the latter was insufficient to enable the authors to determine whether it was the ordinary ($\Delta^9:10$) ethyl oleate or the ethyl *iso*oleate ($\Delta^{10:11}$ or $11:12$) described previously by Moore.³¹

Either copper or nickel may be used to hydrogenate acetaldehyde or to dehydrogenate ethyl alcohol. It is noteworthy that the presence of a trace of water inhibits the former and promotes the latter reaction. The apparent specific volume has been shown by these same investigators to influence the activity of a catalyst: that is to say, a bulky preparation of nickel, or one supported on an inert substance, such as *kieselgühr*, is more active catalytically than a more compact preparation, such as one formed by reduction of the fused oxide. From their numerical results, Armstrong and Hilditch deduce that the catalytic activity of nickel can be satisfactorily explained by a consideration of the surface exposed, and that it is unnecessary to postulate the presence of oxides of nickel in the catalyst.

They have also established that simple ethylenic compounds are hydrogenated, in presence of sufficient nickel, at rates which are in approximately exact proportion to the absolute pressure of the hydrogen. At extremely low concentrations of the catalyst, the increase in rate of hydrogenation becomes less than proportional to the increase in pressure, especially in the cases of multi-ethylenic compounds such as *linolein* or *citral*. On the other hand, the presence of a group in the organic compound which has affinity for nickel, but is not open to hydrogenation, causes the speed of hydrogenation to increase with abnormal rapidity as the hydrogen pressure is increased. Thus the relation between rate of action

³¹ *J. Soc. Chem. Ind.*, 1919, **38**, 320r.

and hydrogen concentration is evidently governed by the type of organic compound present. These results harmonise completely with the view that the process is primarily conditioned by an association of the ethylenic linking with the catalyst, which is itself associated with hydrogen.

W. G. Palmer³² has studied the activity of copper as a catalyst for the dehydrogenation of the lower aliphatic alcohols. He finds that, although electrolytic copper, both when pure and when alloyed with zinc, is catalytically inactive, copper prepared by reduction of its oxide promotes dehydrogenation, although its activity decreases with time. He concludes that the active material is copper in the cuprous form, that the inactivation is due to a slow change of these molecules into the more stable cupric form, and that oxides of copper play no part in the catalysis. The same author in conjunction with (Miss) D. M. Palmer³³ has investigated the reduction of ethylene to ethane with nickel as a catalyst. From their results they infer that a preliminary selective adsorption of hydrogen takes place on the catalyst: thermal contact with ethylene molecules then causes evaporation of hydrogen and any ethane formed, after which ethylene is adsorbed on the catalyst and a nearly steady state of reaction is attained.

Rosenmund, Zetzsche, and Heise³⁴ have developed a theory of the influencing of catalysts by small quantities of other substances. By the addition of minute amounts of suitable promoters or inhibitors they have been able to control the reduction of benzoyl chloride in the presence of palladium or palladinised barium sulphate in such a manner that the chief reaction product may be benzaldehyde, benzyl alcohol, benzyl benzoate, dibenzyl ether, or toluene. The regulating substances were chosen to contain an element of variable valency, among the more important being quinoline, xanthone, dimethylaniline, and particularly quinoline which had been heated with sulphur.

In addition to the reduction of benzoyl chloride, Rosenmund and Zetzsche have studied the dehydrogenation of alcohols in the liquid state.³⁵ All the metals used as catalysts were practically inactive, but addition of quinoline induced specific activity, especially in the cases of copper, nickel, and silver. The best yields of aldehydes are obtained by the catalytic oxidation of an equimolecular mixture of alcohol, quinoline, and *m*-dinitrobenzene in cumene solution in the presence of copper. Secondary alcohols can be similarly

³² *Proc. Roy. Soc.*, 1920, [A], **98**, 13; *A.*, 1920, ii, 609.

³³ *Ibid.*, 1921, [A], **99**, 402; *A.*, ii, 541.

³⁴ *Ber.*, 1921, **54**, [B], 425, 638, 2038; *A.*, ii, 320, 392, 632.

³⁵ *Ibid.*, 1922, 2033; *A.*, ii, 393, 631.

oxidised to ketones, but tertiary alcohols are not attacked by this method.

The use of platinum and palladium both in the colloidal and in the spongy state for catalytic hydrogenation has been shown by Willstätter and Waldschmidt-Leitz³⁶ to depend on the presence of oxygen in the catalyst. According to their view, the catalyst functions alternately as a peroxide (with the metal bivalent) and as a combined hydride and peroxide (with the metal quadrivalent), thus effecting the transfer of hydrogen. By treating their metals in suspension in glacial acetic acid with hydrogen they have obtained inactive catalysts which, however, are easily reactivated by shaking with air. They consider that some, but not all, cases of catalyst poisoning during hydrogenation are due to the gradual removal of the oxygen necessary for catalysis.

Similar results were found in the case of nickel: the lower oxides were catalytically active, but the pure metal, free from oxygen, was inactive until primed with a small quantity of air. Kelber,³⁷ however, carrying out hydrogenations at laboratory temperature, has been unable to confirm these observations in the case of nickel reduced from the carbonate and from the oxalate via the oxide, and has found that his catalyst becomes inactive when shaken with oxygen, and that treatment with hydrogen at 70—80° is then necessary to reactivate it. It seems only fair, however, to point out that Kelber's work was done with sodium cinnamate, whereas Willstätter and Waldschmidt-Leitz used a far greater variety of substances, including benzene, cyclohexene, limonene, pyrrole, phthalic anhydride, *o*-benzylbenzoic acid, and *o*-naphthoylbenzoic acid.

Willstätter and Waldschmidt-Leitz divide unsaturated compounds into three classes, according to the ease with which they are hydrogenated: (a) ethylenic substances, which are reduced so rapidly that the rate of loss of oxygen from the catalyst is negligible in comparison; (b) simple aromatic compounds, which are hydrogenated with much less speed than the olefines, so that loss of oxygen, especially from small amounts of catalyst, may have a marked retarding effect on the velocity of hydrogenation; and (c) other substances, such as polynuclear aromatic compounds, the rate of hydrogenation of which is so small that deoxygenation of the catalyst occurs long before the hydrogenation is complete. In cases of this type, they recommend activation of the catalyst by priming with oxygen from time to time, as suggested by Willstätter and Jaquet.³⁸

³⁶ *Ber.*, 1921, **54**, [B], 113; *A.*, ii, 185.

³⁷ *Ibid.*, 1701; *A.*, ii, 630.

³⁸ *Ibid.*, 1918, **51**, 767; *A.*, 1918, i, 391.

The application of the Nernst heat theorem, using the approximation formula, to the equilibria acetaldehyde, hydrogen, ethyl alcohol; and acetone, hydrogen, isopropyl alcohol, has been carried out by E. K. Rideal,³⁹ who confirms Sabatier's results that nearly complete hydrogenation or dehydrogenation can occur within the small temperature range from 100—350°.

E. B. Maxted,⁴⁰ using platinum and palladium as catalysts for the hydrogenation of oleic acid, has shown that the decrease in activity caused by the poisons lead, mercury, sulphur, arsenic, and zinc is, within the limits zero concentration of the inhibitor nearly to the concentration producing complete inactivation, directly proportional to the concentration of the inhibitor. He has already shown⁴¹ that the occlusive power of palladium for hydrogen varies directly as the content of inhibitor (hydrogen sulphide in this case), so that it follows that the occlusive power for hydrogen varies directly as the catalytic activity. This result he has experimentally demonstrated for catalytic palladium poisoned by lead and using oleic acid as before.⁴² He notes, however, that although the catalytic activity and occlusive power vary lineally with the concentration of the poison, the former property is much more susceptible to poisoning than the latter. In explanation of this, he suggests that whilst catalytic power is mainly a function of surface exposed, occlusion is not confined to the surface.

Carbohydrates.

Much activity has been displayed in the investigation of the carbohydrates, and the long series of researches by Purdie, Irvine, and other workers in the St. Andrews school on the simpler hexoses and their methylated derivatives have paved the way to an understanding of the constitution of some of the more complex members of this group of compounds. The general procedure of fully methylating the complex compound by means of methyl sulphate and sodium hydroxide, followed by methyl iodide and silver oxide, and then of hydrolysing the methylated compounds in which the hydroxyl groups are thus protected, has in several instances proved very successful, inasmuch as the properties of the methylated hexoses which are obtained on hydrolysis are fairly well known. This method is being widely adopted by other workers, and yields more certain results than the investigation of the acyl derivatives

³⁹ *Proc. Roy. Soc.*, 1921, [A], **99**, 153; *A.*, i, 389.

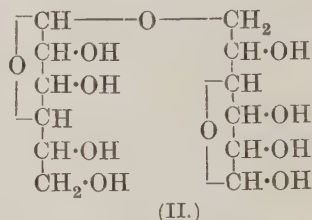
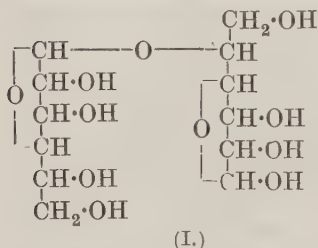
⁴⁰ *T.*, 1920, **117**, 1501; 1921, **119**, 225.

⁴¹ *Ibid.*, 1919, **115**, 1050; 1920, **117**, 1280.

⁴² *Ibid.*, 1921, **119**, 1280.

of the sugars⁴³ or the acetolysis⁴⁴ of polysaccharides by acetyl bromide in the presence of hydrogen bromide and acetic acid, a complex reagent which brings about simultaneous acetylation, hydrolysis, and bromination. Haworth and Hirst⁴⁵ have fully methylated cellobiose, which they obtain in about 30 per cent. yield from cellulose by an improved method of acetolysis. This octamethyl derivative is shown to be heptamethylmethylcellobioside, and splits up on hydrolysis into known butylene-oxidic forms of tetramethyl and trimethyl glucose.

The formula (I) for cellobiose which Haworth and Miss Leitch⁴⁶



suggested during their research on maltose (II) has thus been confirmed.

The constitution of glucal,⁴⁷ which was discussed in last year's Report, has been fully proved and compounds of the type of glucal, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CH}_2$, have been prepared from

other sugars. The names of these, such as rhamnal, lactal, cellobial, etc., have lost their significance as the compounds, when pure, have no aldehydic properties. Glucal itself is oxidised by perbenzoic acid to anhydromannose, which, with alcohol and water, yields mannose and ethylmannoside.

Analogous results have been obtained with rhamnal and cellobial, which incidentally confirm Haworth's formula for cellobiose.

It will be recalled that last year Irvine and Soutar⁴⁸ showed that the yield of pure glucose obtainable from cotton cellulose was, as a minimum, 85 per cent. of the theoretical amount calculated on the basis of the equation $(\text{C}_6\text{H}_{10}\text{O}_5)_n + n\text{H}_2\text{O} = n\text{C}_6\text{H}_{12}\text{O}_6$. Further work by Monier-Williams⁴⁹ has increased the yield of crystalline glucose to more than 90 per cent. and affords strong, although not conclusive, evidence that the molecular unit of unmodified cellulose consists entirely of condensed glucose residues.

⁴³ K. Hess and E. Messmer, *Ber.*, 1921, **54**, [B], 499; *A.*, i, 305.

⁴⁴ M. Bergmann and F. Beck, *ibid.*, 1574; *A.*, i, 649.

⁴⁵ *T.*, 1921, **119**, 193.

⁴⁶ *Ibid.*, 1919, **115**, 809.

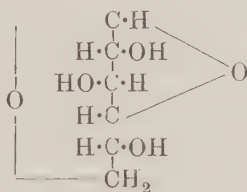
⁴⁷ M. Bergmann and H. Schotte, *Ber.*, 1921, **54**, [B], 440; *A.*, i, 307.

⁴⁸ *T.*, 1920, **117**, 1489.

⁴⁹ *Ibid.*, 1921, **119**, 803.

It has been known for some years that when cellulose or starch is subjected to dry distillation under reduced pressure a well-defined, crystalline compound can be isolated. This was termed by Pictet, its discoverer, *l*-glucosan, and he has argued ⁵⁰ that the formula of this anhydro-glucose must afford a clue to the constitution of cellulose and starch, on the assumption that these are polymerides of *l*-glucosan. Now W. S. Denham ⁵¹ has shown that the limit of methylation of cellulose is practically that required for the formation of trimethyl cellulose, which gives on hydrolysis the same trimethyl glucose isolated by Haworth and Hirst ⁵² from the products of hydrolysis of methylated cellobiose.

The importance, therefore, of ascertaining the constitution of *l*-glucosan is apparent, and Irvine and Oldham ⁵³ have been successful in converting it into a trimethyl glucose identical with that obtained previously from methylglucoside and from maltose, and quite distinct from that obtained (as described above) in two ways from cellulose. It is, however, scarcely a matter of surprise that, considering the complex changes undergone by carbohydrates on heating, the constitution of *l*-glucosan bears no structural relation to that of cellulose. In fact, it has thus been proved that *l*-glucosan is 1 : 6- β -glucose anhydride, and would be designated more correctly as β -glucosan.



Some progress can be recorded in the elucidation of the constitution of starch and the first products of its hydrolysis. The crystalline dextrins first obtained by Schardinger ⁵⁴ in 1903 by the action of certain bacteria (notably *Bacillus macerans*) were investigated by Pringsheim ⁵⁵ and characterised as diamylose ($C_6H_{10}O_5$)₂, triamylose, tetra-amylose, hexa- and octa-amylose, the molecular weights of the acetyl derivatives of these being determined in several solvents. These compounds have been recently investigated further by Karrer ⁵⁶ and his co-workers, who have subjected them to the action of acetyl bromide and acetic acid. In this way,

⁵⁰ Inter alia, *Helv. Chim. Acta*, 1918, **1**, 187.

⁵¹ *T.*, 1921, **119**, 77.

⁵² *loc. cit.*

⁵³ *T.*, 1921, **119**, 1744.

⁵⁴ *Zeit. Nahr. Genusseem.*, 1903, **6**, 865; *A.*, 1904, ii, 67.

⁵⁵ *Ber.*, 1913, **46**, 2959; *A.*, 1913, i, 1156.

⁵⁶ *Helv. Chim. Acta*, 1921, **4**, 169, 678; *A.*, i, 310, 768.

the so-called α -tetra-amylose is converted first into acetylated α -diamylose and then by the opening of the anhydride ring quantitatively into aceto-bromomaltose. It would thus seem that α -amylose is the first known anhydride of a disaccharide.

The methylation of potato starch has been carried out also by Karrer.⁵⁷ The product obtained by the use of methyl sulphate and baryta water has the empirical formula $[C_6H_8O_3(OMe)_2]_n$ with a molecular weight of about 1100, and can be further methylated by means of silver oxide and methyl iodide, giving a methylstarch having a molecular weight in water of about 1200. Solutions of the methylated starch in water or chloroform exhibit the Tyndall effect and under the ultramicroscope show colloidal particles. The aqueous solutions, however, readily undergo ultrafiltration with little loss, and the filtrates appear optically empty and present no Tyndall effect. The size of the starch molecule has not yet been determined and it appears certain that it is much smaller than has been freely suggested by the older workers.

Nitrogen Compounds.

It has been known for some time that an aldehyde in the presence of ammonia can be oxidised to the amide of the corresponding acid. Mignonac⁵⁸ has now shown that alcoholic solutions of aldehydes and ketones can be reduced by hydrogen in the presence of a nickel catalyst to the corresponding amine in accordance with the general scheme, $R \cdot CHO + NH_3 \rightarrow R \cdot CH(OH) \cdot NH_2 \rightarrow R \cdot CH_2 \cdot NH_2$. The reaction appears to be general and possesses the advantage over other methods for the preparation of primary amines in that there is no simultaneous formation of secondary and tertiary amines.

The reaction between secondary bases, formaldehyde, and alcohols or mercaptans has been studied by C. M. McLeod and Mrs. G. M. Robinson.⁵⁹ These authors show that the reaction $NHR_2 + CH_2O + R'OH$ (or $R'SH$) $\rightarrow R_2N \cdot CH_2 \cdot OR'$ + H_2O is quite general; the resulting dialkylaminomethyl alkyl ethers and sulphides, which are best obtained by condensing the components in the cold in the presence of an excess of potassium carbonate, are mobile oils which distil without decomposition. The thio-ethers are more stable than the ethers, but all are more or less readily hydrolysed by water and acids.

Up to the present, methods for the reduction of amino-acids

⁵⁷ *Helv. Chim. Acta*, 1920, **3**, 620; *A.*, 1920, **i**, 820; *ibid.*, 1921, **4**, 185, 263; *A.*, **i**, 311, 313.

⁵⁸ *Compt. rend.*, 1921, **172**, 223; *A.*, **i**, 165.

⁵⁹ *T.*, 1921, **119**, 1470.

with primary amino-groups to the corresponding amino-alcohols have not been available. It has now, however, been found ⁶⁰ that the well-known method of Bouveault and Blanc, in which an ester is reduced with sodium and alcohol, gives, if applied to the acetylated esters of the amino-acids, good yields of the corresponding amino-alcohols. Most of the amino-alcohols thus obtained are now described for the first time and appear to be of considerable physiological interest.

Whilst the substitution of the imino-hydrogen in "saccharin" by alkyl groups entirely destroys the sweetness of that substance, the position is completely reversed in the case of diglycollimide,⁶¹ which, although itself tasteless, yields alkylimides of the general formula $O < \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} > \text{NR}$, which increase in sweetness with an increasing number of carbon atoms up to a maximum in the *N*-propyl derivative. The aryl derivatives, on the other hand, are almost tasteless. These cyclic imide-ethers of diglycollic acid are very hygroscopic and are of little practical importance as sweetening agents, as they are slowly hydrolysed by the absorbed water to the corresponding alkylamine hydrogen diglycollates.

ROBERT H. PICKARD.

PART II.—HOMOCYCLIC DIVISION.

Reactions.

Reduction.—It is remarkable that the catalytic hydrogenation of ω -trifluorotoluene, $\text{Ph} \cdot \text{CF}_3$, should lead exclusively to the production of trifluoromethylcyclohexane, whilst under similar conditions α -difluorotoluene yields difluoromethylcyclohexane together with a small proportion of methylcyclohexane.¹ This stability of fluorine in a side chain towards molecular hydrogen in presence of platinum black is in sharp contrast to the ready removal of the same substituent when attached to the aromatic nucleus, since *p*-fluorobenzoic acid gives first benzoic acid and then cyclohexanecarboxylic acid.

Ethyl α -naphthoate is reduced by sodium and alcohol to a methyl-dihydronaphthalene,² and this reaction recalls the fact that saturated acids can occasionally be reduced to hydrocarbons containing the same number of carbon atoms by means of hydriodic acid and

⁶⁰ P. Karrer, W. Karrer, H. Thomann, E. Horlacher, and W. Mäder, *Helv. Chim. Acta*, 1921, **4**, 76; *A.*, **i**, 228.

⁶¹ M. Sido, *Ber. deut. Pharm.Ges.*, 1921, **31**, 118; *A.*, **i**, 447.

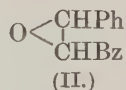
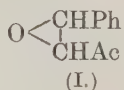
¹ F. Swarts, *Bull. Acad. roy. Belg.*, 1920, 399; *A.*, **i**, 657.

² H. de Pommereau, *Compt. rend.*, 1921, **172**, 1503; *A.*, 1921, **i**, 567.

phosphorus. Undecane, for example, may be obtained in this manner from undecoic acid.³ A device likely to prove useful in many cases is that employed for the reduction of nitropiperonal, which can be effected if the aldehyde group is first protected by condensation with *p*-toluidine and the reduction performed in aqueous alcoholic solution by means of sodium sulphide. The aminoazomethine derivative obtained in this way is then readily hydrolysed by hot water.⁴ An important addition to the methods available for the preparation of arylhydroxylamines consists in the reduction of nitro-compounds in emulsified suspension by means of sodium sulphide.⁵ The process is a modification of that of Willstätter and Kubli,⁶ and the essential novel features are the replacement of ammonium sulphide by sodium sulphide, the employment of aqueous instead of alcoholic solutions, and the production of an emulsion, facilitated by the addition of small amounts of calcium chloride.

Oxidation.—The behaviour of sodium phenoxide at 485–490° in an atmosphere of hydrogen or nitrogen has been examined⁷ and the products are hydrogen, methane or ethane, benzene, diphenyl, diphenyl oxide, 2-hydroxydiphenyl, and larger relative amounts of four dihydroxydiphenyls (2:2', 3:3', 3:4', and probably 2:3').

Novel results have been obtained in an extensive study of the action of hydrogen peroxide in alkaline solution on unsaturated ketones.⁸ In most cases, the product is an ethylene oxide derivative containing one atom of oxygen more than the original ketone. Thus styryl methyl ketone yields β -acetyl- α -phenylethylene oxide (I), m. p. 52–53°, together with a liquid isomeride, and the nature of these substances is placed beyond doubt by the fact that the corresponding compound (II) from phenyl styryl ketone is identical with the product obtained by Widman⁹ by the action of benzaldehyde on ω -bromoacetophenone.



These oxides liberate iodine from potassium iodide and acetic acid with regeneration of the unsaturated ketone, and the compound

³ Krafft, *Ber.*, 1882, **15**, 1697.

⁴ A. Rilliet and L. Kreitmann, *Helv. Chim. Acta*, 1921, **4**, 588; *A.*, i, 567.

⁵ A. Lapworth and (Mrs.) L. K. Pearson, *T.*, 1921, **119**, 765, 768.

⁶ *Ber.*, 1908, **41**, 1936.

⁷ F. Hofmann and M. Heyn, *Brennstoff-Chem.*, 1921, **2**, 147; *A.*, i, 506.

⁸ E. Weitz and A. Scheffer, *Ber.*, 1921, **54**, [B], 2344; *A.*, i, 869; *ibid.*, 2327; *A.*, i, 868.

⁹ *A.*, 1913, i, 1220.

(I) is transformed by hydrogen chloride in acetic acid into an oily chlorohydrin which slowly liberates hydrogen chloride, with formation of hydroxymethylenebenzyl methyl ketone, $\text{OH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{COMe}$.

Halogenation.—A comparison ¹⁰ of the activity of catalysts in the chlorination of benzene by sulphuryl chloride has shown that anhydrous aluminium chloride is by far the most efficient, the yield of monochlorobenzene amounting to nearly 90 per cent. of the theory in some experiments.

It is, perhaps, a little remarkable that the dibromination of ethylbenzene should lead to $\alpha\beta$ -dibromoethylbenzene,¹¹ which, by the action of magnesium, is converted into styrene.

Etherification and Esterification.—The very useful process of etherification of phenols by means of arylsulphonic esters has been examined in detail so as to determine the optimal conditions,¹² and workers who have occasion to alkylate phenolic bases especially should make themselves familiar with the results. The preparation of many benzyl derivatives, benzyl esters, ethers, phenylacetone, nitrile, benzylamines, etc., is found to proceed in aqueous solution so as to give far higher yields than those obtained in other ways.¹³

Replacement of Substituents in Aromatic Compounds.—Improvements have been made in the already numerous processes for the replacement of halogen in benzene and naphthalene derivatives by hydroxyl.¹⁴ It is found that the salt of a weak acid can often replace the alkali usually employed; thus an 83 per cent. yield of salicylic acid is obtained when potassium *o*-chlorobenzoate is heated with water, sodium acetate, and a trace of cupric acetate at 140–150°. Partly successful attempts have been made to apply similar reactions to the replacement of halogens by sulphur and selenium and by the sulphonic and arsinic acid groups.

Thionbenzoyl Derivatives.—The only known substance containing the group $\cdot\text{CSCl}$ is thiocarbonyl chloride, and special interest attaches, therefore, to the preparation ¹⁵ of thionbenzoyl chloride, $\text{Ph}\cdot\text{CSCl}$, which may be obtained as a reddish-violet, mobile liquid, b. p. 60–62°/0.2 mm., of disagreeable odour, by the action of thionyl chloride on dithiobenzoic acid. The substance behaves as a true acid chloride, yielding an anilide and methyl thionbenzoate, $\text{Ph}\cdot\text{CS}\cdot\text{OMe}$, by the action of aniline and methyl alcohol respectively. For comparison, the isomeric methyl thiobenzoate, $\text{Ph}\cdot\text{CO}\cdot\text{SMe}$, was prepared from benzoyl chloride and methyl mercaptan. Thion-

¹⁰ O. Silberrad, *T.*, 1921, **119**, 2029.

¹¹ J. von Braun and K. Moldanke, *Ber.*, 1921, **54**, [B], 618; *A.*, i, 405.

¹² Z. Földi, *Ber.*, 1920, **53**, [B], 1839; *A.*, 1920, i, 877.

¹³ M. Gomberg and C. C. Buchler, *J. Amer. Chem. Soc.*, 1920, **42**, 2059; *A.*, 1920, i, 839.

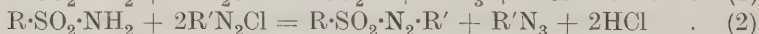
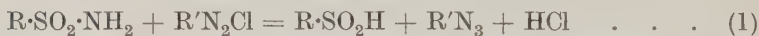
¹⁴ K. W. Rosenmund and H. Harms, *Ber.*, 1920, **53**, [B], 2226; *A.*, i, 103.

¹⁵ H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, 1920, **3**, 824; *A.*, i, 25.

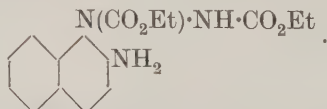
benzoyl chloride yields benzoyl chloride and monoclinic sulphur when heated at 110—120° in a current of oxygen.

Diazonium Salts.—The researches of Meldola and others have made us familiar with the fact that a diazo-group has a loosening effect on ortho-substituents, and that this property is much enhanced when there is a positive ¹⁶ group situated in the ortho- or para-position with respect to the affected radicle. Thus the diazotisation of dinitroanilines ($\text{NH}_2 : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 3$ or $1 : 2 : 5$) frequently leads to the formation of diazo-oxides. Numerous methods have been suggested with the object of avoiding this difficulty, and the latest device,¹⁷ which apparently works well, is to diazotise the feeble base in acetic acid solution at a low temperature with a solution of sodium nitrite in sulphuric acid monohydrate. Even 2 : 4 : 6-trinitroaniline can be diazotised and 2 : 4 : 6-trinitro-*m*-phenylenediamine tetrazotised by this method. The 2 : 4 : 6-trinitrobenzenediazonium salt is unusually reactive and couples with mesitylene to form 2 : 4 : 6-trinitrobenzeneazomesitylene, $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_2\text{Me}_3$,¹⁸ which may be reduced to mesidine.

A curious reaction which may be employed for the preparation of the arylsulphinic acids and aromatic azoimides occurs when, for example, benzenediazonium chloride is allowed to react with an alkaline solution of *p*-toluenesulphonamide.¹⁹ The process is a fairly general one, results in high yields, and may be carried out in accordance with either of the equations (1) or (2) :



Hydrazine Derivatives.—Sodium hyposulphite gives excellent results in the reduction of diazo-salts, and *p*-nitrophenylhydrazine may be prepared in this way from *p*-nitroaniline in a yield amounting to 95 per cent. of the theoretical.²⁰ The action of azodicarboxylic ester on β -naphthylamine leads to the production of 2-amino-1-dicarbethoxyhydrazinonaphthalene,²¹



¹⁶ By this term are implied the groups like $-\text{NO}_2$, $-\text{CO}_2\text{H}$, $-\text{SO}_2\text{H}$, etc., usually called negative. Their true character as positive groups has in recent years been emphasised by Fry, Lapworth, Vorländer, and others. It is true that such groups have a negative effect on the atom to which they are united.

¹⁷ E. Misslin, *Helv. Chim. Acta*, 1920, **3**, 626; *A.*, 1920, *i*, 887.

¹⁸ K. H. Meyer and H. Tochtermann, *Ber.*, 1921, **54**, [B], 2283; *A.*, *i*, 895.

¹⁹ P. K. Dutt, H. R. Whitehead, and A. Wormall, *T.*, 1921, **119**, 2088.

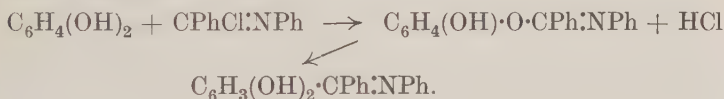
²⁰ L. Thomson, *J. Soc. Dyers and Col.*, 1921, **37**, 7; *A.*, *i*, 133.

²¹ O. Diels, *Ber.*, 1921, **54**, [B], 213; *A.*, *i*, 280.

Condensations.—The condensation of acetylene with benzene in presence of aluminium chloride gives $\alpha\alpha$ -diphenylethane and 9:10-dimethylantracene hydride in approximately equal proportions, along with traces of styrene.²² Toluene gives *as*-di-*p*-tolylethane, 2:7-dimethylantracene, and smaller relative amounts of 2:6-dimethylantracene, β -methylantracene, xylene, mesitylene, and ψ -cumene. Chlorobenzene gives as chief product di-*p*-chloro-*s*-diphenylethane, $C_6H_4Cl \cdot CH_2 \cdot CH_2 \cdot C_6H_4Cl$.

Nitriles are increasingly employed for the synthesis of phenolic ketones, and a whole series of acyl resorcinols and phloroglucinols has been prepared²³ by condensing the phenols with aliphatic nitriles according to the method devised by Hoesch.²⁴ These substances are remedies against the tape-worm; the resorcinol derivatives are as useful as those derived from phloroglucinol, and the most valuable acid residue appears to be *isohexoyl*. A mixture of cyanogen and hydrogen chloride reacts as the dichlorodi-imide of oxalic acid, and with resorcinol in ethereal solution condenses to products which yield resorecylglyoxylic acid, $C_6H_3(OH)_2 \cdot CO \cdot CO_2H$, and 2:4:2':4'-tetrahydroxybenzil, $C_6H_3(OH)_2 \cdot CO \cdot CO \cdot C_6H_3(OH)_2$, along with other substances on hydrolysis.²⁵ Orcinol gives only the glyoxylic acid derivative.

Benzanilideiminochloride and its derivatives substituted in the nucleus condense readily with resorcinol, apparently in accordance with the scheme:—



The first reaction occurs at 100° and the isomeric change at about 150°, the final product being readily hydrolysed by dilute hydrochloric acid with formation of benzo-resorcinol.²⁶ This process is analogous to Hoesch's synthesis and also to Dimroth's preparation of β -resorecylaldehyde by the hydrolysis of the anilide resulting from the interaction of resorcinol, formanilide, and phosphoryl chloride in ethereal solution.²⁷ The latter method has now been applied with good results to the preparation of alkylaminobenzophenones, replacing the resorcinol by a tertiary amine and the formanilide by a benzanilide.²⁸ The substances formerly described by other

²² O. W. Cook and V. J. Chambers, *J. Amer. Chem. Soc.*, 1921, **43**, 334; *A.*, i, 332.

²³ P. Karrer and S. Rosenfeld, *Helv. Chim. Acta*, 1921, **4**, 707; *A.*, i, 793.
²⁴ *Ber.*, 1915, **48**, 1122.

²⁵ P. Karrer and J. Ferla, *Helv. Chim. Acta*, 1921, **4**, 203; *A.*, i, 341.

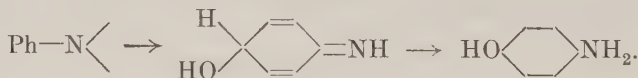
²⁶ H. Stephen, *T.*, 1920, **117**, 1529.

²⁷ Dimroth, Zöppritsch, *Ber.*, 1902, **35**, 995.

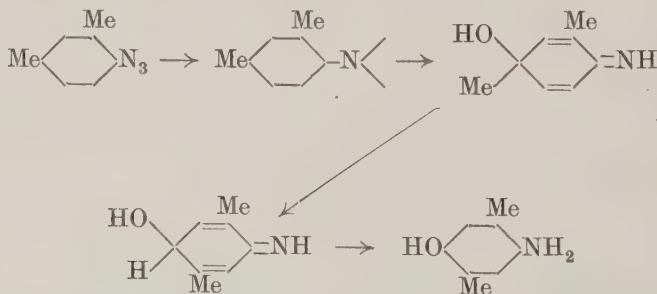
²⁸ J. Meisenheimer, E. von Budkewicz, and G. Kananow, *Annalen*, 1921, **423**, 75; *A.*, i, 356.

authors as dialkylaminobenzophenones are actually benzanilides. Dimethylaminobenzophenone has been employed for the preparation of leucotriphenylmethane dyes of the type RR_1R_2CH in the hope of resolving some member of the class and determining the question of the survival or disappearance of optical activity after oxidation and subsequent reduction. Racemisation is certainly to be anticipated.

The Transformations of Arylhydroxylamines.—It is impossible adequately to discuss in this Report the voluminous experimental work of Bamberger²⁹ on this subject, but some reference at least is necessary to the careful comparison drawn between the behaviour of an arylhydroxylamine and the corresponding arylazide towards sulphuric acid under various conditions. The results are closely parallel with the significant exception that azoxy-compounds, frequently obtained from the hydroxylamines, are never produced from the azides. This disposes of the suggestion which has been put forward³⁰ that the parallelism is due to preliminary conversion of the azide into the hydroxylamine by loss of nitrogen and hydration. Bamberger considers that the transformations are best explained by the formation of an arylimide, $Ar-N<$, from the hydroxylamine by loss of water and from the azide by loss of nitrogen. The formation of aminophenol then occurs as follows:—



One further example may be illustrated, the conversion of *m*-xylylazide into 2-amino-*p*-5-xenol:—



Of the numerous further reactions, reduction leads to aniline derivatives and hydrolysis to dihydroxybenzenes, reduction and hydrolysis to phenol derivatives. The arylimide may also add on

²⁹ *J. pr. Chem.*, 1921, [ii], **102**, 267; *A.*, i, 716; *Annalen*, 1921, **424**, 233; *A.*, i, 716; *ibid.*, 297; *A.*, i, 723.

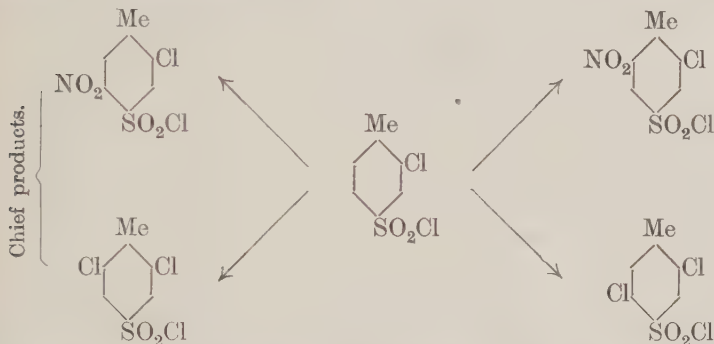
³⁰ Friedländer and Zeitlin, *A.*, 1894, i, 184.

an alcohol, resulting in the production of phenolic ethers. The somewhat more complex problem of the changes induced by halogen acids is also discussed.

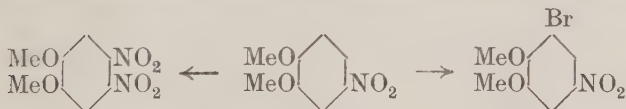
Substitution and Orientation.

The nitration of benzotrichloride to *m*-nitrobenzotrichloride was referred to in the Report for the year 1919, and it is now found that the very stable ω -trifluorotoluene also yields on nitration the *m*-nitro-derivative as chief product.³¹ These results are in agreement with the principle of induced latent polarity of atoms in a chain which was also discussed in the Report for the year 1919.

The examination³² of the nitration and chlorination of 2-chloro-*p*-toluenesulphonyl chloride has given results which may be summarised in the scheme:—



This may be compared with the behaviour of 4-nitroveratrole:—



There is evidently a general tendency for the entrance of halogen to be definitely directed by positive groups to the meta-position to a greater extent than is the case when the entering substituent is nitroxyl.

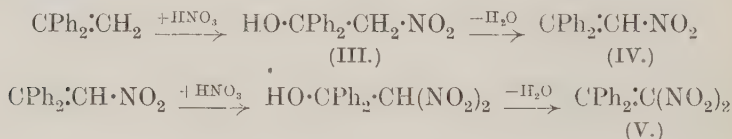
The effect of chloro- and nitro-groups on the mobility of other similar substituents has been exhaustively investigated by Hollemann and his collaborators³³ in the case of the dichlorodinitro-

³¹ F. Swarts, *Bull. Acad. roy. Belg.*, 1920, 389; *A.*, i, 656.

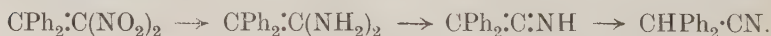
³² W. Davies, *T.*, 1921, 119, 853.

³³ A. F. Hollemann, A. I. den Hollander, and F. E. van Halften, *Rec. trav. chim.*, 1921, 40, 323; *A.*, i, 503; A. F. Hollemann and F. E. van Haeften, *ibid.*, 67; *A.*, i, 167; E. J. E. Hüffer, *ibid.*, 451; *A.*, i, 549; A. F. Hollemann, *Rec. trav. chim.*, 1920, 39, 736; *A.*, i, 102.

benzenes, the six trichloronitrobenzenes, the six trichlorodinitrobenzenes, the three tetrachlorobenzenes, pentachlorobenzene, and hexachlorobenzene. In general, the results obtained in studying the action of sodium methoxide are in harmony with previous experience, although some novel features are brought to light. Most interesting is the fact that the reactivity of a chlorine atom is enhanced by the entrance of a second chlorine atom in the meta-position. It will be recalled that Wieland and Sakellarios³⁴ showed that ethylene is capable of nitration to β -nitroethyl nitrate and, in correcting an earlier publication relating to the action of nitric acid on $\alpha\alpha$ -diphenylethylene, Anschütz³⁵ discloses the interesting fact that Kekulé had in 1877 reached the opinion that nitroethyl nitrate is the product of the action of nitric acid on ethylene. The course of the nitration of diphenylethylene in glacial acetic acid solution is shown in the scheme :—



III, IV, and V are isolated and the latter undergoes reduction in the following manner :—



The nitration of ethylene derivatives has also been studied by Wieland³⁶ in continuation of his comprehensive researches. The substance (III) above is obtained by the action of a solution of absolute nitric acid in carbon tetrachloride on diphenylethylene at -10° . In some cases the primary product cannot be isolated, thus the action of nitric acid on β -methyl- Δ^3 -butylene, $\text{CMe}_2\text{:CHMe}$, leads immediately to the nitro-derivative, $\text{CMe}_2\text{:CMe}\cdot\text{NO}_2$, mixed with some nitroisomyl nitrate.

These observations are, of course, extremely instructive in relation to the mechanism of substitution in aromatic compounds which by analogy are due to reactions of addition and fission. During the past year Kurt H. Meyer has emphasised the addition theory of diazo-coupling³⁷ and his views will meet with general support in most respects, but he appears to think that the gap in auxochromic or activating power existing between Me and OMe involves no necessity for a special explanation. Nevertheless, the existence of

³⁴ *A.*, 1920, i, 280.

³⁵ Anschütz and Hilbert, *Ber.*, 1921, **54**, [B], 1854; *A.*, i, 783.

³⁶ H. Wieland and F. Rahn, *ibid.*, 1770; *A.*, i, 782.

³⁷ *Ibid.*, 2265; *A.*, i, 855.

conjugated ethylene-nitrogen and ethylene-oxygen systems can scarcely be disputed, and Meyer does not dispose of or even contemplate the possibility that the unsaturated system in phenols and amines includes the oxygen or nitrogen atoms.³⁸ This would, after all, be a mere extension of the assumption already made in order to explain ortho- and para-substitution by reference to the length of the unsaturated chain to which addition occurs.

Geometrical Isomerism.

A third monobromostyrene has been prepared,³⁹ and the isomerides are obtained by the following methods. (A), m. p. 6—7°, by heating sodium dibromo- β -phenylpropionate with an aqueous solution of sodium carbonate; (B), m. p. — 43°, by the action of hydrogen bromide on phenylacetylene; (C), m. p. — 8 to — 7°, by heating phenyl bromostyryl ketone, $\text{CHPh}:\text{CBr}:\text{COPh}$, with powdered sodium hydroxide. A and C (the new isomeride) both give $\alpha\beta\beta$ -tribromoethylbenzene on bromination, whereas B gives $\alpha\alpha\beta$ -tribromoethylbenzene. A and C are therefore stereoisomerides of the formula $\text{CHPh}:\text{CHBr}$. Auto-oxidation of the substance B yields ω -bromoacetophenone as the result of an intramolecular rearrangement.⁴⁰ The two ω -bromostyrenes are very sensitive to light and either alone or mixed are converted to a substance or mixture with a constant melting point of 2°.⁴¹

Gentle isomerisation of safrole, $\text{CH}_2\text{O}_2:\text{C}_6\text{H}_3:\text{CH}_2:\text{CH}:\text{CH}_2$, by means of dilute alcoholic potassium hydroxide at 82—86° produces a new unstable *cis*-isosafole, $\text{CH}_2\text{O}_2:\text{C}_6\text{H}_3:\text{CH}:\text{CH}:\text{CH}_3$, readily transformed by alkali at a higher temperature into the known *trans*-modification.⁴² The isomerides can be interconverted through their dibromides and related monobromo*isosafoles*, the latter yielding the *isosafoles* on reduction with zinc and ethyl alcohol. It is stated that the *isosafole* dibromides are optically active, but this must surely be an error, especially since safrole is always isolated from essential oils containing active constituents.

Formylphenylacetanilide, prepared from phenylacetanilide and formic ester by the action of sodium wire in ethereal suspension, has been isolated⁴³ in two forms, m. p. 68° and m. p. 98°, which are apparently not desmotropic, but the geometrical isomerides

³⁸ Since writing the above, a paper in the December number of the *Berichte* has been consulted, in which Auwers criticises the views of Meyer and points out that physical data strongly support the hypothesis of the existence in phenols of conjugated systems which include the oxygen atom.

³⁹ C. Dufraisse, *Compt. rend.*, 1920, **171**, 960; *A.*, i, 17.

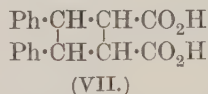
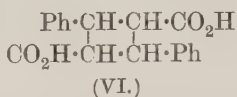
⁴⁰ *Idem, ibid.*, 1921, **172**, 162; *A.*, i, 168. ⁴¹ *Idem, ibid.*, 67; *A.*, i, 104.

⁴² Shoichiro Nagai, *J. Coll. Eng. Tokyo*, 1921, **11**, 83; *A.*, i, 857.

⁴³ W. Wislicenus and R. Erbe, *Annalen*, 1920, **431**, 119; *A.*, 1920, i, 841.

of the enol modification, $\text{HO}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}\cdot\text{NHPh}$. The related piperidides have also been prepared and exhibit a similar behaviour.

The formulæ VI and VII for saturated dimerides of cinnamic acid allow for the existence of eleven isomerides, five corresponding with VI and six with VII.



The isolation of a seventh truxillic acid ⁴⁴ proves for the first time that these substances belong to both series depicted. It is proposed to term the dimerides of *trans*-cinnamic acid truxillic acids as formerly, and for those derived from *cis*-cinnamic acid the name truxinic acids is adopted. β -Truxinic acid, which itself results from the illumination of *cis*-cinnamic acid, yields the new isomeride, neotruxinic acid, by the prolonged action of aqueous pyridine at 160—170°. The acid has also been found to occur in small amount among the truxillic acids obtained during the preparation of cocaine.

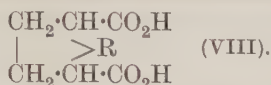
In the tetrahydronaphthalene series, the method of condensation with acetone is found to distinguish between *cis*- and *trans*-diols, only the former giving dioxymethylene derivatives.⁴⁵ Nevertheless, the diagnostic value of the reaction has its limits, since both *cis*- and *trans*-1 : 2-cycloheptanediols yield isopropylidene ethers.⁴⁶ The oxidation of cycloheptene by means of potassium permanganate and magnesium sulphate yields *cis*-1 : 2-cycloheptanediol, m. p. 46°, whilst the *trans*-compound, m. p. 63°, is obtained by the use of peroxybenzoic acid in chloroform solution followed by the action of dilute hydrochloric acid. An ingenious and novel device has been evolved ⁴⁷ in order to determine the configurations of the two $\alpha\alpha'$ -dibromoadipic acids, $\text{CO}_2\text{H}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, m. p.'s 193° and 139°. The method is probably of general applicability, and depends on the replacement of the bromine atoms by a bivalent group so as to produce a ring. The product typified by the expression VIII will be obtained in the *cis*- or *trans*-modification according as the starting point is respectively the meso- or racemic form of the dibromo-acid, and if RH_2 is a symmetrical molecule, only the

⁴⁴ R. Stoermer and E. Laage, *Ber.*, 1921, **54**, [B], 77; *A.*, i, 179; R. Stoermer and F. Scholtz, *ibid.*, 85; *A.*, i, 180; R. Stoermer and E. Laage, *ibid.*, 96; *A.*, i, 182.

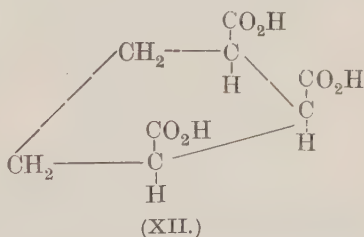
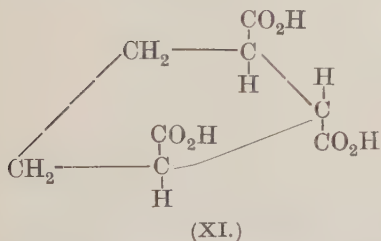
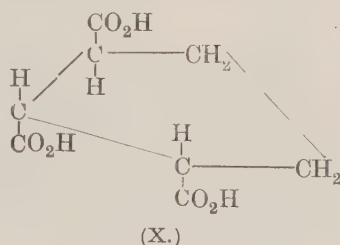
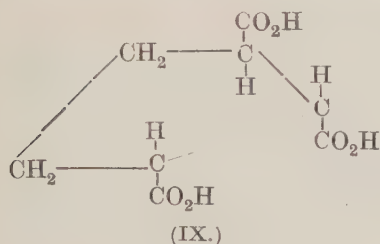
⁴⁵ J. Böeseken and H. G. Derx, *Rec. trav. chim.*, 1921, **40**, 519; *A.*, i, 663.
⁴⁶ *Idem*, *ibid.*, 529; *A.*, i, 663.

⁴⁷ W. H. Perkin and E. Robinson, *T.*, 1921, **119**, 1392.

trans-modification will be resolvable into optically active components,



The diethyl ester of the dibromoadipic acid, m. p. 193° , is a readily purified solid and condenses with the sodium derivative of malonic ester to a tetracarboxylic ester which by the usual processes yields *cyclopentane-1:2:3*-tricarboxylic acid. This substance could be resolved with the aid of brucine, and the acid, m. p. 193° , is therefore the racemic modification of dibromoadipic acid. In order to make the argument clear, all possible configurations of the *cyclopentanetricarboxylic acid* are given below :



X is the mirror image of IX, whilst XI and XII have superposable mirror images. Consequently, the acid obtained as described above is the inactive mixture of IX and X, and reference to the models will show that these configurations are directly related to those of dextro- and lævo- $\alpha\alpha'$ -dibromoadipic acid.

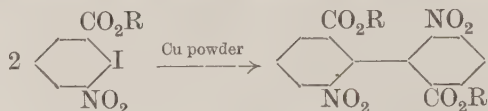
The existence of a peculiar form of isomerism in the diphenyl series, exemplified at present only in the case of the two *oo*-dinitrobenzidines and their derivatives,⁴⁸ has been confirmed by the isolation of two 6 : 6'-dinitrodiphenic acids.⁴⁹ The first isomeride, m. p. 297° or 303° , was already known and was obtained by Schulze⁵⁰

⁴⁸ J. C. Cain, A. Coulthard, and (Miss) F. M. G. Micklethwait, *T.*, 1912, **101**, 2298; *ibid.*, 1913, **103**, 2074; J. C. Cain and (Miss) F. M. G. Micklethwait, *ibid.*, 1914, **105**, 1437, 1442.

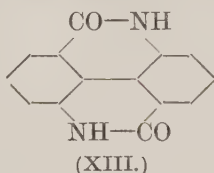
⁴⁹ J. Kenner and W. V. Stubbings, *ibid.*, 1921, **119**, 593.

⁵⁰ *Annalen*, 1880, **203**, 95.

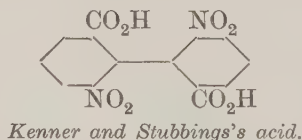
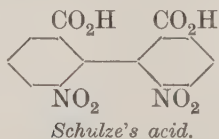
as one of the products of the nitration of diphenic acid as also by the oxidation of the mixture of dinitrophenanthraquinones. It yields a diamino-acid on reduction, and may be converted into 2 : 2'-dinitrodiphenyl or into carbazole. Further details of information in regard to this acid will be welcomed. The new isomeride, m. p. 263° , is obtained as an ester, in accordance with the scheme :—



The behaviour of the acid on reduction is in sharp contrast with that of Schulze's substance, since a dilactam (XIII) is the sole product.



The suggestion is, therefore, that the substances are stereoisomerides of the annexed configurations :



The assignment of these formulæ is made on the basis of the ring formation already referred to, but as an additional argument in favour of their correctness it should be noted that the particular methods of formation of the isomerides might be expected to lead to the observed results. The opening of the phenanthrene ring naturally leaves the carboxyl groups in something analogous to a *cis*-position, whilst the repulsion of similar groups accounts for the production of a substance possessing a *trans*-spatial character.

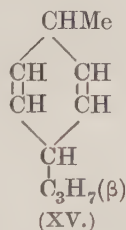
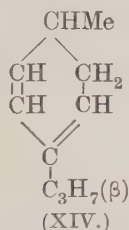
A fourth benzildioxime may be obtained by the addition of ammonium chloride to a solution of α -benzildioxime in aqueous sodium hydroxide which has been allowed to remain during two hours.⁵¹ δ -Benzildioxime melts at 220° and is rapidly converted in alcoholic solution by acids or ammonia into the α -isomeride (m. p. 237°). It is characterised by the formation of a buff-coloured nickel compound, which passes with facility into the red nickel compound of α -benzildioxime and is thus differentiated from the

⁵¹ F. W. Atack and L. Whinyates, *T.*, 1921, **119**, 1184.

similar nickel compound of γ -benzildioxime. The constitution of this interesting substance has not yet been fully elucidated, but its existence cannot be explained by the conventional Hantzsch-Werner hypothesis unless this be extended by the admission of the possible existence of structural isomerides. Attack considers ⁵² that the isomerism in the group of the oximes is more probably structural than geometrical and in a general discussion of the subject makes out a strong case in support of his thesis. It is not, however, yet possible to regard the problem as solved, although it is clear that the stereochemical theory in its simplest form is inadequate.

Natural Products.

A new monocyclic terpene has been found ⁵³ in the oil of *Mosla japonica*, Maxim. Moslene nitrosochloride on treatment with sodium ethoxide yields among other products an azo-compound identical with that obtained by the reduction of 2-nitro-*p*-cymene. From this and other considerations it may be deduced that moslene must have the constitution (XIV) or (XV)



Later ⁵⁴ the terpene was proved to exist in other essential oils containing *p*-cymene.

Piperitone, the peppermint ketone of eucalyptus oils, has been investigated and characterised by numerous derivatives. It has the formula $\text{C}_{10}\text{H}_{16}\text{O}$ ⁵⁵ and may be oxidised to thymol by ferric chloride or catalytically reduced to menthone. Another paper ⁵⁶ deals with its characteristic benzyldiene and other derivatives and contains a brief account of the relation of the occurrence of piperitone to the botanical characters of the genus *Eucalyptus* and to the other oil constituents.

The oil from the grass *Andropogon Jwarancusa*, Jones, contains a ketone, $\text{C}_{10}\text{H}_{16}\text{O}$, to the extent of about 80 per cent. of the whole,

⁵² *T.*, 1921, 119, 1175.

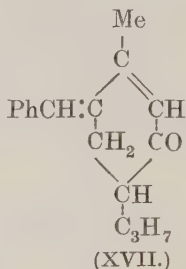
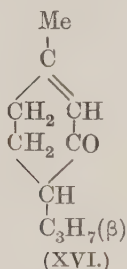
⁵³ Y. Murayama, *J. Pharm. Soc. Japan*, 1921, 769; *A.*, i, 875.

⁵⁴ *Idem*, *ibid.*, No. 475, 786; *A.*, i, 875.

⁵⁵ Smith and Penfold, *J. Proc. Roy. Soc. N.S. Wales*, 1920, 54, 40.

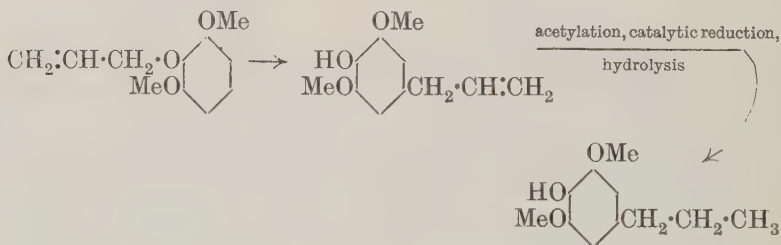
⁵⁶ J. Read and H. G. Smith, *T.*, 1921, 119, 779.

the identity of which with *d*-piperitone⁵⁷ is considered to be beyond doubt.⁵⁸ A conclusive proof is afforded that this grass-oil ketone is *d*- Δ^1 -*p*-menthen-3-one (XVI) and its benzylidene derivative is represented by the formula (XVII)



There is of course no difficulty in accepting the latter suggestion in view of the well-known fact that unsaturated atoms are efficient transmitters of the activating influence of a carboxyl group. The constitution (XVI) has also been assigned to piperitone from eucalyptus oil in view of the observation that this substance may be oxidised to 2-hydroxy- Δ^1 -menthen-3-one.⁵⁹

Pikamar, a constituent of beechwood tar, has been synthesised⁶⁰ by an application of the Claisen transformation and thus shown to be 4-hydroxy-3:5-dimethoxy-*n*-propylbenzene. The synthesis is illustrated in the annexed scheme:—



A crystalline constituent of Siamese benzoin termed lubanyl benzoate is apparently the benzoate of coniferyl alcohol having the constitution



⁵⁷ Piperitone occurs, however, in an inactive form in eucalyptus oils.

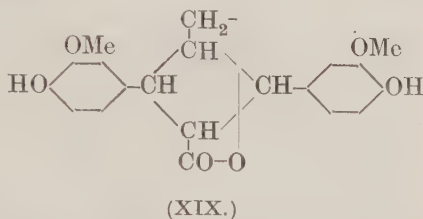
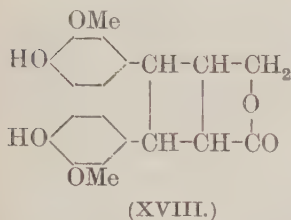
⁵⁸ J. L. Simonsen, *T.*, 1921, **119**, 1644.

⁵⁹ L. Givaudan & Co., *Perf. Essent. Oil Rec.*, 1921, **12**, 80; *A.*, i, 793.

⁶⁰ F. Mauthner, *J. pr. Chem.*, 1921, [ii], **102**, 36; *A.*, i, 726.

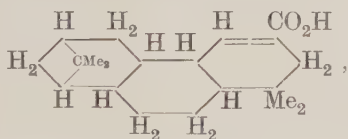
but the actual isolation of the alcohol has hitherto proved impossible on account of its instability to alkali and acid.⁶¹

The liquors from the sulphite-cellulose process contain a crystalline lactone, $C_{20}H_{20}O_6$, which may be obtained by extraction with ether. The constitution XVIII or XIX is suggested for this substance as the result of a study of its transformations,⁶²



and of these, XVIII is probably to be preferred in view of the proved structure of guaiaretic acid. The substance is of interest as constituting another member of the growing class of di-eugenol derivatives.

The resin acids have been the subject of several communications, of which a theoretical paper on the constitution of abietic acid may be mentioned as containing some important suggestions.⁶³ The formula evolved for abietic acid is



and this is derived from the condensation of a molecule of α -pinene with one of β -pinene followed by oxidation of a methyl group to carboxyl. This is a line of argument which is sure to be fundamentally sound, but the particular interpretation does not square very well with the results of other work which now falls to be discussed. O. Aschan⁶⁴ has isolated and carefully characterised a new crystalline resin acid, pinabietic acid, $C_{20}H_{30}O_2$, from the less volatile fractions obtained on distilling pine oil in a current of superheated steam. The constitutional investigation conducted by

⁶¹ A. Zinke and J. Dzimal, *Monatsh.*, 1920, **41**, 423; *A.*, i, 187; F. Reinitzer, *Arch. Pharm.*, 1921, **259**, 60; *A.*, i, 352.

⁶² B. Holmberg, *Svensk Kem. Tidskrift*, 1920, **32**, 56; *A.*, i, 25; *Ber.*, 1921, **54**, [B], 2389; *A.*, i, 849; B. Holmberg and M. Sjöberg, *ibid.*, 2406; *A.*, i, 850.

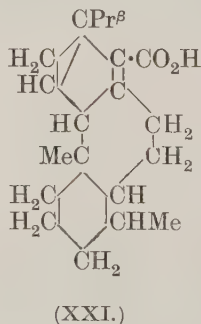
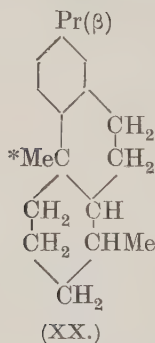
⁶³ Ad. Grün, *Zeit. Deut. Öl. Felt-ind.*, 1921, **41**, 49; *A.*, i, 344.

⁶⁴ *Annalen*, 1921, **424**, 117; *A.*, i, 669.

A. I. Virtanen ⁶⁵ has given the following results. Pinabietic acid contains one double bond (saturated dibromide and dihydro-derivative) and one bridged ring (dihydrobromide).

In spite of the fact that the acid can be nitrated and sulphonated, the presence of an aromatic nucleus is improbable on account of the empirical composition, the behaviour towards the reagents for the double bond, and also in view of the values obtained for the refractive powers of the esters. The latter are difficult to prepare, and also to hydrolyse when once formed.

Pinabietyl chloride evolves carbon monoxide and hydrogen when distilled under reduced pressure and furnishes a hydrocarbon, $C_{19}H_{28}$, called pinabietene. The latter contains an aromatic nucleus and is octahydromethylretene, since it may be changed to retene by heating with sulphur, the reaction involving the loss of hydrogen and a methyl group. Further, the oxidation of pinabietene by nitric acid or by manganese dioxide and sulphuric acid produces benzene-1 : 2 : 4-tricarboxylic acid. The formulæ suggested for pinabietene and pinabietic acid are XX and XXI respectively, although it is admitted that the positions of the double bonds; cross-linking and methyl group marked with an asterisk, are still doubtful.

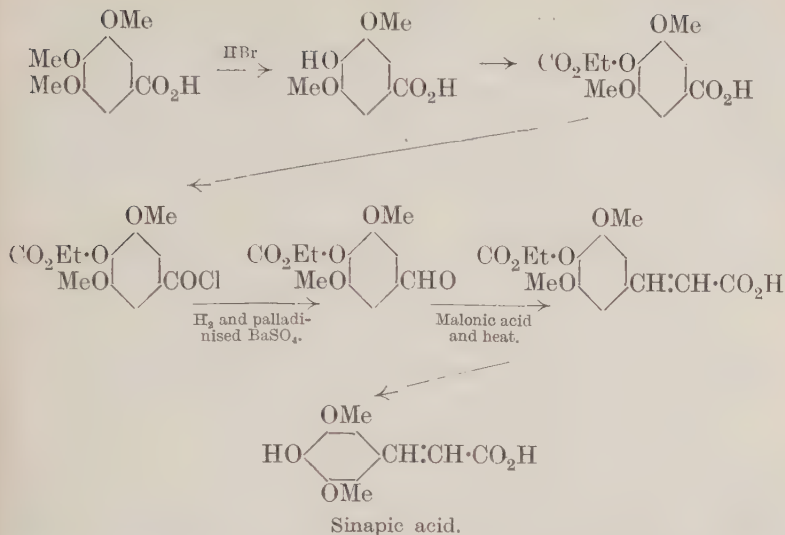


But the arguments cited are not at all conclusive, and that some modifications may be expected is clear from the fact that the above structures cannot be subdivided into units containing the arrangement of carbon atoms present in isoprene. This is possible in the case of all known substances of proved constitution which have a relation to the terpene series.

The synthesis of sinapic acid ⁶⁶ has been effected through the stages :—

⁶⁵ *Annalen*, 1921, **424**, 150; *A.*, i, 669.

⁶⁶ E. Späth, *Monatsh.*, 1920, **41**, 271; *A.*, i, 28.



Sinapic acid was then converted into sinapin iodide, identical with the salt of natural sinapin, by condensing acetylsinapoyl chloride with dimethylaminoethanol to β -dimethylaminoethyl acetylsinapate, which by gentle hydrolysis yielded the corresponding sinapate. The addition of methyl iodide now furnished sinapin iodide, $\text{NMe}_3\text{I}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{OH}$, thus confirming Gadamer's formula for sinapin.

Alicyclic Group.

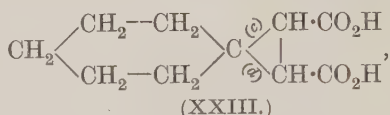
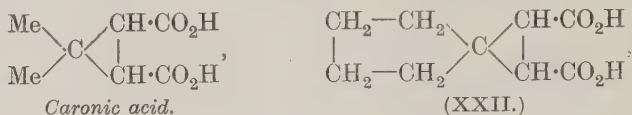
It is quite impossible owing to limitations of space adequately to summarise the work of Thorpe, Ingold, Kon, and others on the related topics of the conditions governing the ease of formation and the stability of cyclic systems, and indeed a consideration of this group of papers emphasises the desirability of the system of publication from time to time of résumés by the original workers themselves of the position arrived at in the study of their problems. The theory that an alteration in the angle subtended by two of the valencies of a carbon atom involves a corresponding alteration in that enclosed by the remaining two has been again experimentally verified.⁶⁷ It is suggested that "if 2β be the angle formed by the valencies a and b , the angle 2θ between the directions taken up by the valencies c and d will be determined by the condition that these directions are equally inclined to each other and to the directions

⁶⁷ O. Becker and J. F. Thorpe, *T.*, 1920, **117**, 1579.

occupied by the valencies a and b . If 2β is known, it is shown that 2θ can be calculated by means of the equation

$$\cos \theta = \frac{1}{4}(\sqrt{\cos^2 \beta + 8} - \cos \beta).$$

It must be pointed out that the experimental results support the sense of this assumption, but are not as yet capable of being brought into any quantitative relation with it. In the series



a and b are taken to be the valencies represented at the left of the quaternary carbon atom, and we may examine the effect of alterations in the angle between a and b by study of the stability of the cyclopropane ring. It has already been shown⁶⁸ that in the case of the cyclohexane derivative XXIII the cyclopropane ring is unusually stable and resists the action of concentrated hydrochloric acid at 240° , whereas caronic acid is attacked readily and even at 200° by 5 per cent. acid. Here the enlargement of the normal angle between a and b renders the angle between the valencies c and d in (XXIII) smaller without strain and consequently the cyclopropane ring is more stable. Now the angle in a symmetrical cyclopentane ring differs from the normal angle between unstrained carbon valencies by about $18'$ only, and the substance (XXII) should therefore from the present point of view closely resemble caronic acid in respect of the stability of its cyclopropane ring. This was found to be the case, and the distinction in properties between XXII and XXIII is unexceptionable evidence in favour of the fundamental theory. Other comparisons were instituted with similar results.

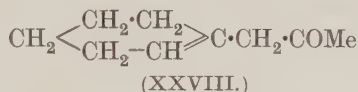
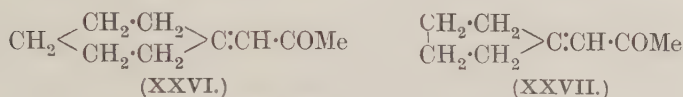
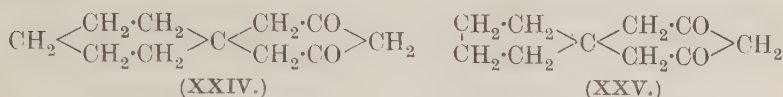
Progress has been made⁶⁹ in the attempt to synthesise spiro-hydrocarbons which on account of their simplicity may be expected to furnish valuable evidence relating to the nature of valency as it occurs in carbon compounds.

Up to the present, the dihydroresorcinol derivatives (XXIV) and (XXV) have been prepared by the addition of ethyl sodio-malonate to the unsaturated ketones (XXVI) and (XXVII) followed by hydrolysis of the products. The success of this process

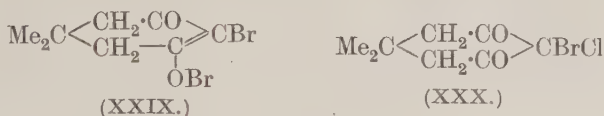
⁶⁸ C. K. Ingold and J. F. Thorpe, *T.*, 1919, **115**, 320.

⁶⁹ W. S. G. P. Norris and J. F. Thorpe, *ibid.*, 1921, **119**, 1199.

proves that the condensation product of *cyclohexanone* and acetone has the constitution figured (XXVI), and not that (XXVIII) ascribed to it by Wallach on the ground of optical properties. The substance is a true analogue of mesityl oxide, and it is remarkable that it does not exhibit the usual exaltation of refractive power associated with endocyclic compounds and with $\alpha\beta$ -unsaturated ketones.



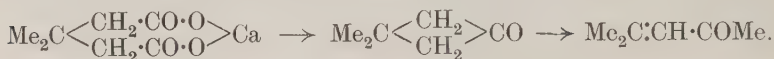
Another incidental result of the work under discussion is the disposal of Vorländer's somewhat bizarre conception that the dibromo-derivative of dimethyldihydroresorcinol should be formulated as a bromoxy-compound (XXIX). The bromination and subsequent chlorination and vice versa of dimethyldihydroresorcinol yield one and the same substance, which has accordingly the constitution (XXX).



The ready elimination by means of alkali of one halogen atom from these and similar substances in the form of a hypobromite is referred to the general tendency to acquire a hydrogen atom necessary for tautomerism. The pronounced electropositivity of bromine in α -bromo-ketones is, however, a very general phenomenon, and is exhibited in cases such as ethyl bromoacetoacetate where the possibility of tautomerism already exists. The polar character of the bromine follows from the principle of induced latent polarity of atoms, but even so the gap in reactivity existing between the first and second bromine atoms certainly requires explanation.

Ingold (see below) has pointed out that the *gem*-dialkyl group has a remarkable effect in promoting the formation of cyclic structures, and it is found on calculation that the $\beta\beta$ -dialkylglutaric acids occupy intermediate positions between glutaric and adipic acids in respect of the stability of cyclic ketones into which they

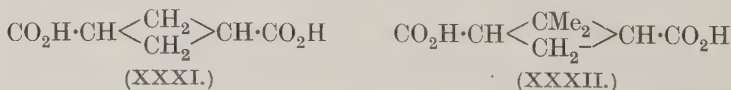
might be converted by distillation of their calcium salts. Actually it was found that the *cyclobutanones* were formed, but at the high temperature of the reaction underwent isomerisation. Thus $\beta\beta$ -dimethylglutaric acid yielded mesityl oxide.



Other *gem*-dialkylglutaric acids behaved similarly, but no trace of unsaturated ketone could be obtained from the calcium salts of glutaric acid and of β -methylglutaric acid.⁷⁰

C. K. Ingold has published a series of important researches on the subject of the conditions underlying the formation of unsaturated and cyclic compounds, which he prefaces in the first paper⁷¹ by an account of a new and very interesting hypothesis relating to the calculation of the angles between carbon-to-carbon valencies. He suggests that the atoms joined to a carbon atom may be considered to occupy spherical domains, the cubic contents of which are proportional to the atomic volume of the element. These spheres are presumed to be in mutual contact and also with an internal sphere, and if now the centres of two of the external spheres are joined, the angle between the valencies is that subtended by this line at the centre of the internal sphere. These angles are readily calculated, and in a polymethylene chain the angle between carbon-to-carbon valencies is nearly 6° greater than has hitherto been supposed.

A very interesting result which follows is that the ease of formation of polymethylenes should be in the order *cyclohexane* > *cyclopentane* > *cyclopropane* > *cyclobutane* > *cycloheptane*. This is in excellent agreement with thermochemical data and general chemical experience, especially the difficulty of producing *cyclobutane* derivatives. The powerful ring-promoting properties of the *gem*-dialkyl grouping is easily accounted for on these lines, although it still remains a mystery why the *cyclobutanedicarboxylic acid* (XXXI) should be so easily obtained, and many attempts to synthesise norpinic acid (XXXII) have always failed.



Some striking instances of the effect are recalled; the fact that all known β -lactones contain the *gem*-dimethyl grouping, the stability of $\beta\beta$ -dimethylglutaric anhydride, and the observation of Perkin and Thorpe that $\alpha\beta\beta$ -trimethylglutaric anhydride crystallises from water with solvent of crystallisation.

In adopting a plan of campaign with the object of testing this

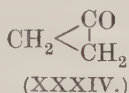
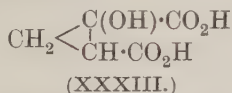
⁷⁰ G. A. R. Kon, *T.*, 1921, **119**, 810.

⁷¹ *Ibid.*, 305.

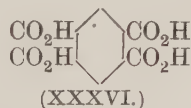
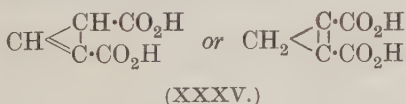
theory of the effect of atomic volumes on valency-to-valency angles, it was thought desirable to study a reaction which proceeds partly to a cyclic substance and partly in other directions, and the action of alkali hydroxides on α -bromo-dibasic acids was chosen. The normal products are a cyclic compound, an unsaturated substance, and a hydroxy-derivative. A detailed study of the action of concentrated sodium hydroxide on α -bromoglutaric acid and $\alpha\alpha'$ -dibromoglutaric acid, diethyl α -bromo-glutaconate,⁷² α -bromoadipic acid, and $\alpha\alpha'$ -dibromoadipic acid⁷³ has been carried out and considerable experimental difficulties overcome in the isolation of a large proportion of the total product. The results are in general agreement with the theory, but do not lend themselves to summarisation in view of the large number of side reactions encountered.

Some compounds of novel type were prepared in the course of the work. Among these may be mentioned *cyclopropanoldicarboxylic acid* (XXXIII), obtained by the action of aqueous sodium carbonate on dimethyl $\alpha\alpha'$ -dibromoglutarate. The first product is the corresponding bromo-acid.

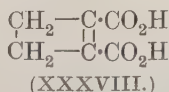
XXXIII yielded *cyclopropanone* (XXXIV) by the action of concentrated sulphuric acid. The ketone was characterised by its semicarbazone.



Ethyl bromoglutaconate was prepared by the action of diethylaniline on glutaconic ester dibromide, and this substance or $\alpha\beta$ -dibromoglutaric acid, on treatment with alkali, gave rise among other substances to *cyclopropenedicarboxylic acid* (XXXV) and *pyromellitic acid* (XXXVI).



The stereoisomeric dibromo- and di-iodo-adipic esters, on boiling with 2*N*-sodium carbonate, gave good yields of muconic acid (XXXVII), which is thus for the first time an available substance, whilst a small yield of *cyclobutene-1:2*-dicarboxylic acid (XXXVIII) resulted under the same conditions from the so-called racemic esters only.



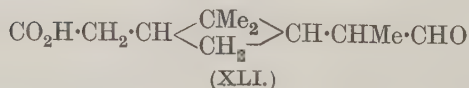
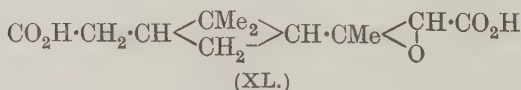
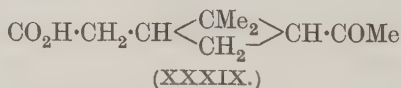
⁷² E. H. Farmer and C. K. Ingold, *T.*, 1921, **119**, 2001.

⁷³ C. K. Ingold, *ibid.*, 951.

The configurations employed by Ingold for the dibromoadipic acids are different from those arrived at by the method already described (see above), but as they are deduced from the related tetrahydrofurandicarboxylic acids, the possibility of the occurrence of a Walden inversion must be taken into account. In order to harmonise the results, the Walden inversion would be required to occur in the case of the replacement of one bromine atom only, or, of course, there could be a double inversion in the one series and inversion at only one of the asymmetric carbon atoms in the other. In any case, the further investigation of the problem would be of much interest.

Pinene Derivatives.—Very considerable progress towards the goal of the complete synthesis of pinene has been recorded ⁷⁴ and this most important of all terpenes can now be produced from pinonic acid (XXXIX).

Ethyl *r*-pinonate condenses with ethyl chloroacetate in presence of sodium ethoxide to a glycidic ester, from which the acid XL is obtained on hydrolysis. The latter substance is converted on heating at 230° in a vacuum to the semi-aldehyde of homopinocamporic acid (XLI), readily oxidised to homopinocamporic acid (XLII). Thence *r*-pinocampphone (XLIII) is obtainable by applying the Dieckmann reaction. α -Pinene (XLIV) has been already obtained by Tschugaeff ⁷⁵ from the corresponding alcohol, pinocampeol, by the xanthogenate reaction and now from a pinocampylamine by the method of exhaustive methylation.⁷⁶ The base employed in the latter process is a stereoisomeride of the known pinocampylamine of Wallach and of Tilden, and is obtained by the hydrogenation of pinylamine, which latter is proved ⁷⁷ to be a β -pinene derivative (XLV). It does not appear to have been actually prepared from pinocampphone.

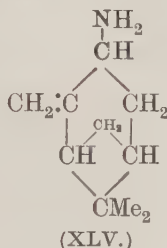
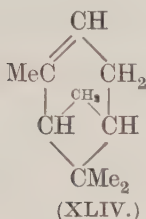
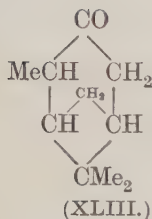
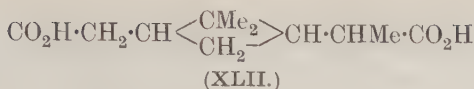


⁷⁴ L. Ruzicka and H. Trebler, *Helv. Chim. Acta*, 1921, **4**, 666; *A.*, i, 796.

⁷⁵ *A.*, 1908, i, 93.

⁷⁶ L. Ruzicka and H. Trebler, *Helv. Chim. Acta*, 1920, **3**, 756; *A.*, i, 36.

⁷⁷ *Ibid.*, 1921, **4**, 566; *A.*, i, 573.



It has been demonstrated ⁷⁸ that the action of dry hydrogen chloride on pinene at low temperatures does not yield bornyl chloride, but a true pinene hydrochloride, which is a liquid. This *tert.*-pinene hydrochloride is only stable below -10° , and in the absence of cooling changes spontaneously to solid bornyl chloride with evolution of heat.

Polynuclear Types.

Hydrindene Group.—Hydrindene itself has not previously been closely studied. It can be easily obtained in quantity by the hydrogenation of crude indene,⁷⁹ and its behaviour resembles that of tetrahydronaphthalene. A very large number of diketohydrindenes have been prepared by condensing aromatic hydrocarbons with dimethyl- and diethyl-malonyl chlorides with the aid of aluminium chloride.⁸⁰ The observation that diethylmalonyl chloride is far more suitable than the dimethyl compound for the preparation of alkylated diketohydrindene derivatives from phenolic ethers is perhaps an example of the application of Ingold's hypothesis which is discussed above.

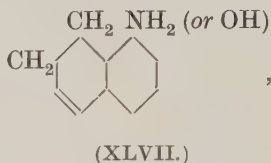
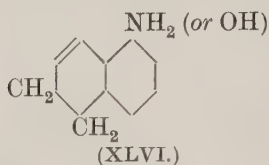
Naphthalene Group.—Hydrogenated naphthalene derivatives have engrossed much attention recently, partly, no doubt, because tetrahydronaphthalene is now an article of commerce. The important discovery made by Rowe and referred to last year, that the reduction of naphthalene by means of sodium and alcohol leads to Δ^2 -dihydronaphthalene, which is only hydrogenated further after isomerisation to the Δ^1 -isomeride, has been found to have its parallel in the cases of the reduction of α -naphthylamine and

⁷⁸ O. Aschan, *Öfvers. Finska Vet.-Soc.*, 1914, **57**, [A], No. 1, 35 pp.; *A.*, 1921, i, 795.

⁷⁹ W. Borsche and M. Pommer, *Ber.*, 1921, **54**, [B], 102; *A.*, i, 168.

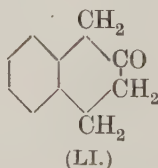
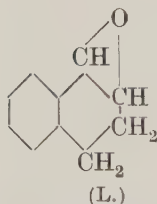
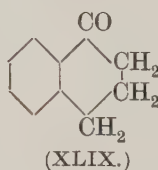
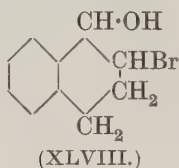
⁸⁰ K. Fleischer, *Annalen*, 1921, **422**, 231; *A.*, i, 251; K. Fleischer and F. Seifert, *ibid.*, 272; *A.*, i, 254.

α -naphthol.⁸¹ In each case a 5:8-dihydro-derivative is first formed and subsequently isomerised by the action of a sodium alkoxide solution at a suitable concentration and temperature. It is not known whether the Δ^1 -derivatives produced in this series of experiments are 5:6- or 7:8-dihydro-compounds (XLVI and XLVII),



but apparently only one of these is obtained. Theoretical considerations indicate the second alternative as most probably the correct representation of the constitution of these substances.

The work of Rowe on the reduction of naphthalene has been confirmed by F. Straus and L. Lemmel, who have made a very thorough study of the transformations of Δ^1 -dihydronaphthalene⁸² so as to compare the behaviour of the substance with that of propenylbenzene. The dibromide of the hydrocarbon yields 2-bromo-1-hydroxynaphthalene (XLVIII) by the action of magnesium carbonate in aqueous acetone. This substance may be oxidised to a bromo-ketone yielding 1-keto-tetrahydronaphthalene (XLIX) on reduction. On the other hand, the bromohydrin (XLVIII) is converted by alcoholic potassium hydroxide to an ethylene oxide (L), which is transformed into 2-keto-tetrahydronaphthalene (LI) by treatment with dry hydrogen chloride.



Δ^1 -Dihydronaphthalene dibromide may be conveniently obtained

⁸¹ F. M. Rowe and (Miss) E. Levin, *T.*, 1920, **117**, 1574; 1921, **119**, 2021.

⁸² F. Straus and L. Lemmel, *Ber.*, 1921, **54**, [B], 25; *A.*, i, 170; F. Straus and A. Rohrbecker (and, in part, L. Lemmel), *ibid.*, 40; *A.*, i, 171.

by the bromination of tetrahydronaphthalene,⁸³ and the dihydronaphthalene readily obtained by the action of zinc and alcohol on the dibromide. If, however, the alcohol is replaced by a non-hydroxylic solvent, an energetic reaction leads to the production of several compounds; among them the polymeride, $(C_{10}H_{10})_8$, a yellow powder. The action of sulphuric acid on a solution of the dihydronaphthalene in a hydrocarbon results in dimerisation to a crystalline product, m. p. 93° , together with oily isomerides.

A very ingenious attempt⁸⁴ to provide a synthetic substitute for the higher fatty acids depends on the catalytic reduction of α -naphthoyl-*o*-benzoic acid, $C_{10}H_7 \cdot CO \cdot C_6H_4 \cdot CO_2H$. This compound is potentially sufficiently cheaply prepared to meet the end in view, since it requires only naphthalene as the organic starting point. The acid is reduced by hydrogen in presence of oxygenated platinum to four stereoisomeric perhydro- α -naphthylmethylbenzoic acids, $C_{10}H_{17} \cdot CH_2 \cdot C_6H_{10} \cdot CO_2H$, a dihydro-acid containing the carbonyl group representing an isolable intermediate stage. The perhydro-acids have the constitution of stearic acid less six hydrogen atoms from positions 1, 6, 8, 12, 17, 17 due to the three rings contained, and their alkali salts are soaps corresponding approximately with those derived from fatty acids containing ten carbon atoms. The alkaline earth and heavy metal salts are soluble in hydrocarbons. In this connexion it may be mentioned that in the course of an extensive research which may ultimately indicate an entirely new method of constitutional analysis, W. B. Hardy has shown that no cyclic compound is an efficient lubricant of a bismuth to bismuth surface.⁸⁵

Gattermann's synthesis of hydroxyaldehydes from phenols and hydrogen cyanide in presence of hydrogen chloride and zinc chloride, followed by hydrolysis of the aldimine hydrochloride, has been applied to the ten dihydroxynaphthalenes,⁸⁶ all of which undergo the synthesis, with production of thirteen (possibly more) dihydroxynaphthaldehydes, only one of which had previously been accurately described. The introduction of the substituent was found to proceed according to established rules, 2-naphthols being reactive in the 1-position and 1-naphthols in the 4-position and to a smaller extent in the 2-position. Curiously enough, 1 : 5-dihydroxynaphthalene gives the *p*-hydroxyaldehyde only, whilst 1 : 8-dihydroxynaphthalene gives rise to both *o*- and *p*-derivatives, the latter in very much greater relative amount. The oxidation of 1 : 7-dihydroxynaphthalene by means of lead peroxide in benzene

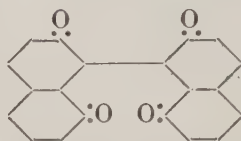
⁸³ J. von Braun and G. Kirschbaum, *Ber.*, 1921, **54**, [B], 597; *A.*, i, 407.

⁸⁴ R. Willstätter, D.R.-P. 325714; *A.*, i, 177; R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, 1921, **54**, [B], 1420; *A.*, i, 667.

⁸⁵ *Phil. Mag.*, 1920, [vi], **40**, 201; *A.*, 1920, ii, 534.

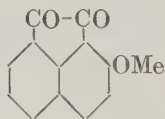
⁸⁶ G. T. Morgan and D. C. Vining, *T.*, 1921, **119**, 177.

suspension produces mainly a carbonate and a small yield of a dinaphtha-1 : 7-1' : 7'-diquinone, probably of the annexed constitution

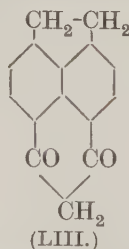


The diquinone forms a yellow, additive compound with benzene, $C_{20}H_{10}O_4 \cdot C_6H_6$, whilst the benzene-free compound crystallises in pale orange tablets which become bright red at 160° , reverting to the original colour on cooling.⁸⁷ No adequate account is possible here of Morgan and Smith's researches on the constitution of simple and complex cobaltic lakes of various naphthaquinoneoximes,⁸⁸ but the subject must not be passed without an appreciative reference to a very successful application of the co-ordination theory. The paper is one which must be consulted in the original by all those who are interested in the problems of valency theory.

Acenaphthene Group.— β -Methoxyacenaphthenequinone (LII) is readily obtained by the condensation of β -naphthyl methyl ether and phenyloxaliminochloride with the help of aluminium chloride,⁸⁹ but this otherwise useful synthesis is not of general applicability.



(LII.)



(LIII.)

Pericyclic derivatives of acenaphthene are not numerous, but may be obtained by the one-stage indanedione synthesis mentioned above. The most interesting example is that of the substance (LIII) prepared by the action of aluminium chloride on a mixture of malonyl bromide and acenaphthene in carbon disulphide solution.⁹⁰

Anthracene Group.—As usual, there has been much activity evinced in the preparation of substituted anthraquinones, and the

⁸⁷ G. T. Morgan and D. C. Vining, *T.*, 1921, **119**, 1707.

⁸⁸ *Ibid.*, 704.

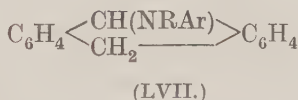
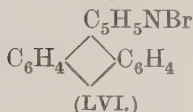
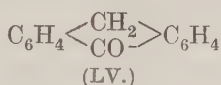
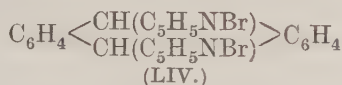
⁸⁹ H. Staudinger, H. Goldstein, and E. Schlenker, *Helv. Chim. Acta*, 1921, **4**, 342; *A.*, i, 433.

⁹⁰ K. Fleischer, H. Hittel, and P. Wolff, *Ber.*, 1920, **53**, [B], 1847; *A.*, 1920, i, 853.

results are on the whole in accord with previous experience and scarcely call for special attention. The various dibromoanthraquinones have been carefully oriented⁹¹ and the conclusion has been reached that the dibromoanthraquinone employed by Graebe and Liebermann in the synthesis of alizarin must have been the 2 : 3- or 2 : 7-isomeride.

The products of the dinitration of anthraquinone are shown to be 1 : 5- (37 per cent.), 1 : 8- (37 per cent.), 1 : 7- (4·2 per cent.), 1 : 6- (3·6 per cent.), 2 : 6- (6 per cent.), 2 : 7- (4 per cent.), leaving only 8·2 per cent. unaccounted for and certainly due in part to losses in manipulation. The literature in this field contains the record of different results and the work under discussion will clear the air.⁹²

Some novel results are recorded in a paper⁹³ which contains *inter alia* a description of a convenient process for the preparation of anthrone. Anthracene dibromide reacts with pyridine to form 9 : 10-dihydroanthraquinyldipyridinium dibromide (LIV), which yields anthrone (LV) in quantitative yield on boiling with water.



The action of sodium hydroxide (or aliphatic amines) and of aromatic amines leads to the production of the stable anthranilylpyridinium salt (LVI) and the reduced derivative (LVII) respectively. Scholl has proved⁹⁴ that the deep violet-blue compounds exhibiting striking fluorescences which Schaarschmidt⁹⁵ obtained by the reduction of 1-benzoylanthraquinones with aluminium or copper powder in concentrated sulphuric acid solution are actually a new class of compounds containing tervalent carbon. The product from 1-*p*-chlorobenzoylanthraquinone crystallises in violet-blue needles, m. p. 253°, and is represented as shown below. It is unimolecular in boiling nitrobenzene and has unsaturated properties, combining, for example, with *p*-benzoquinone just as triphenylmethyl does.

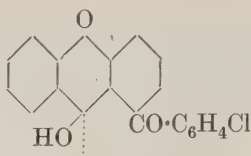
⁹¹ M. Battegay and J. Claudin, *Bull. Soc. Ind. Mulhouse*, 1920, **86**, 632; *A.*, i, 349; Grandmougin, *Compt. rend.*, 1921, **173**, 717; *A.*, i, 871.

⁹² M. Battegay and J. Claudin, *Bull. Soc. Ind. Mulhouse*, 1920, **86**, 628; *A.*, i, 350.

⁹³ E. de Barry Barnett and J. W. Cook, *T.*, 1921, **119**, 901.

⁹⁴ *Ber.*, 1921, **54**, [B], 2376; *A.*, i, 872.

⁹⁵ *A.*, 1915, i, 566, 696; 1916, i, 408.



A reference may be made in this section to the surprising production of dihydrophenanthrene by the action of bromine on phenanthrene in glacial acetic acid solution in presence of sodium acetate.⁹⁶

New Polynuclear Types.—The pyrogenic distillation of 1-phenylindene induces isomerisation to a new hydrocarbon not identical with 2-phenylindene.⁹⁷ The substance may be a *cyclobutane* derivative having either of the constitutions



The main product of the thermal decomposition of acenaphthene is acenaphthylene (LVIII), but many other substances are formed⁹⁸ including colourless leucacene, which crystallises from benzene as the compound $4\text{C}_{54}\text{H}_{32}, 5\text{C}_6\text{H}_6$, violet rhodacene, bronze-red chalkacene, polyacenaphthylene, $\text{C}_{264}\text{H}_{176}$, and three chromacenes, one of which is black.

To chalkacene the formula (LIX) is assigned, and rhodacene is apparently regarded as a quinonoid form of the same arrangement of nuclei. Rhodacene is obtained by boiling leucacene with nitrobenzene, whereby acenaphthylene (2 mols.) is split off at the same time.



The formula of rhodacene contains four tervalent carbon atoms marked *a*, *b*, *c*, *d* in the chalkacene formula (LIX) and if this is really correct it is not surprising that isomerisation to chalkacene takes place under the influence of light or on continued boiling in nitrobenzene.

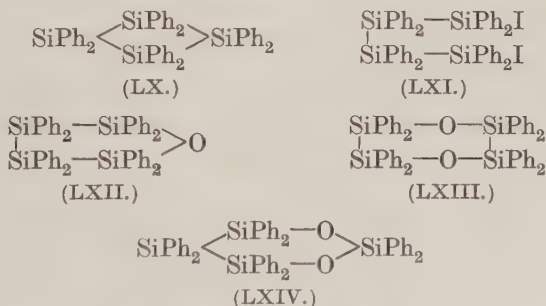
⁹⁶ F. Mayer and A. Sieglitz (with W. Ludwig), *ibid.*, [B], 1397; *A.*, i, 554.

⁹⁷ H. Henstock, *T.*, 1921, **119**, 1461.

⁹⁸ K. Dziewonski (with J. Podgórska, Z. Lemberger, and J. Suszka), *Ber.*, 1920, **53**, [B], 2173; *A.*, i, 105.

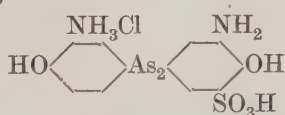
Compounds containing Silicon, Arsenic, and Metals.

The action of sodium on diphenylsilicon dichloride is complex and results in the production of three crystalline compounds, two of which have been examined, as well as other substances.⁹⁹ The crystalline compounds both give values in molecular-weight determinations approximating to those required for the formula Si_4Ph_8 . One of the substances is saturated, but the other readily forms an iodide, $\text{Si}_4\text{Ph}_8\text{I}_2$, and an oxide, $\text{Si}_4\text{Ph}_8\text{O}$. A second oxide, $\text{Si}_4\text{Ph}_8\text{O}_2$, is the result of the action of boiling nitrobenzene on the unsaturated silicohydrocarbon, whereas the isomeride crystallises unchanged from this solvent. No little difficulty is experienced in assigning formulæ to these substances, for the composition in each case suggests the constitution (LX). The iodide and oxide would then have the formulæ (LXI) and (LXII), whilst the dioxide is considered to be either (LXIII) or (LXIV). The isomerism of the "saturated" and "unsaturated" silicohydrocarbons may, it is thought, be explained on the basis that they are both octaphenyl-silicotetranes having silicon atoms in coplanar and tetrahedral arrangements respectively.



Much attention has been devoted to organic compounds of phosphorus, arsenic, antimony, and bismuth, but on account of limitations of space even some outstanding results cannot be discussed.

H. King¹ has tracked down the sulphur-containing constituent of salvarsan prepared by the hyposulphite reduction method and finds it to be 3 : 3'-diamino-4 : 4'-dihydroxy-5-sulphoarsenobenzene monohydrochloride,



⁹⁹ F. S. Kipping and J. E. Sands, *T.*, 1921, **119**, 835.

¹ *Ibid.*, 1107, 1415.

The new *o*-aminophenolsulphonic acid which can be obtained by hydrolysis of this arsenobenzene derivative has been synthesised, and the mechanism of the introduction of the sulphonic group is an interesting problem.

The application of the diazo-synthesis to the production of aryl-arsinic² and aryl-stibinic³ acids has been studied with valuable results, including the determination of the optimal conditions for the reaction; thus, for example, in the case of the arsinic acids the alkalinity of the solution should be regulated so that the process can occur in accordance with the equation:—



In the case of the stibinic acids, the solution may be alkaline, and a really convenient process for the production of aryl antimony derivatives is available. The aryl-stibinic acids are apparently derived from a polymerised antimonious acid, and are pronouncedly colloidal in their properties. Phenylstibine tetrachloride, PhSbCl_4 , is obtained from phenylstibinic acid by the action of concentrated hydrochloric acid; on heating, it dissociates into chlorine and phenyldichlorostibine, PhSbCl_2 , and the latter undergoes further decomposition with the production of diphenylchlorostibine, Ph_2SbCl , and antimony chloride. The action of sulphurous acid on phenylstibinic acid leads to phenylstibinic oxide, PhSbO , and more energetic reduction produces stibiobenzene, $\text{PhSb}:\text{SbPh}$, which is a brown, amorphous powder very susceptible to atmospheric oxidation.

A large number of arylbismuthine derivatives have been prepared⁴ by applications of the Grignard reaction and from bismuth haloids and mercury diaryls. Thus bismuth bromide and mercury diphenyl interact with production of triphenylbismuthine in quantitative yield.

Triaryl bismuthines react as a rule with bismuth haloids to produce diarylbismuthine haloids, but tri- α -naphthylbismuthine and bismuth bromide yield α -naphthylbismuthine dibromide in whatever proportion they are mixed.

The preparation of lead *tricyclohexyl* as a crystalline substance of molecular weight corresponding in dilute solution with the formula $\text{Pb}(\text{C}_6\text{H}_{11})_3$ places beyond doubt the existence of tervalent lead in organic compounds.⁵ The substance is obtained by the addition of lead chloride to a solution of magnesium *cyclohexyl* bromide

² H. Schmidt, *Annalen*, 1920, **421**, 159; *A.*, 1920, i, 897.

³ *Idem*, *ibid.*, 174; *A.*, 1920, i, 900.

⁴ F. Challenger and C. F. Allpress, *T.*, 1921, **119**, 913.

⁵ R. Krause, *Ber.*, 1921, **54**, [B], 2060; *A.*, i, 825.

in ether, and is readily converted by iodine into lead tricyclohexyl iodide. In view of its unsaturated character the compound is compared with triphenylmethyl.

I desire to thank Miss M. Jobson, M.A., B.Sc., for much assistance in drawing up the foregoing report. The period covered includes December 1920 and 1921.

R. ROBINSON.

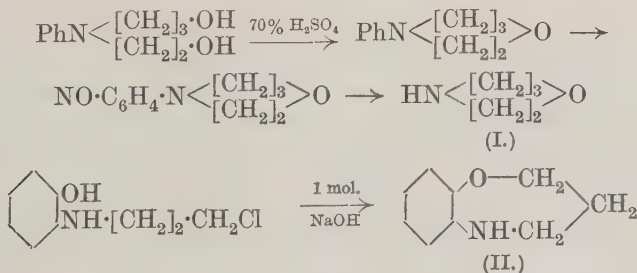
PART III.—HETEROCYCLIC DIVISION.

ALTHOUGH the general level of interest of the work published this year is perhaps somewhat lower than that dealt with last year, a very small proportion is such that it can reasonably be passed unnoticed in an Annual Report. This fact, with a decided increase in the volume of work published, and the Reporter's desire to supply sufficient detail for a reasonable grasp of the topics reviewed in the limited space at his disposal, must explain any terseness of expression.

Ring Formation.

The synthetical operations recorded during the period under review afford a number of illustrations of the various influences which affect the process of ring formation; these it seems preferable to consider collectively rather than under the separate classes of compounds from which they are drawn.

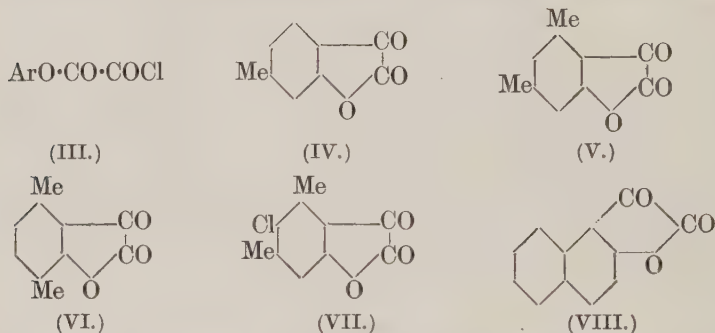
The syntheses of the seven-membered rings contained in homomorpholine (I) and its benzo-derivative (II) are of the usual type, but require careful adherence to special conditions and furnish very moderate yields : ¹



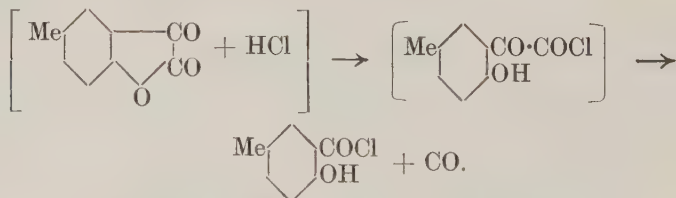
The products, however, which are strongly basic, when once obtained do not exhibit any particular instability.

¹ J. von Braun and O. Braunsdorf, *Ber.*, 1921, **54**, [B], 685; *A.*, i, 435.
E 2*

It would appear that the influences, familiarly grouped under the term "steric," have much less influence on intramolecular than on intermolecular reactions.² Thus, by the action of aluminium chloride on the requisite oxalyl chlorides, of the type (III), the coumarandiones (IV—VIII) are readily obtained.³ The formation of 5-methylcoumarandione (IV) rather than its 3-methyl isomeride is not necessarily due to steric causes, since the alkyl group in such reactions is known to exert a para-directive influence. The presence of the methyl group in the meta-position to the oxygen atom has an important influence on the result, comparable with



its favourable influence on the stability of coumaranones.⁴ Thus, from phenyloxalyl or *p*-tolylloxalyl chloride, in place of coumarandiones, *o*-hydroxybenzoyl chlorides and carbon monoxide are produced :



In connexion with this interesting reaction, it is worth noting that oxalyl chloride itself is decomposed by aluminium chloride into carbonyl chloride and carbon monoxide,⁵ and that no signs of para-compounds could be detected among the products from phenyloxalyl chloride. These facts, together with the well-known tendency of aluminium chloride to effect hydrolysis, suggest that the products in brackets may represent intermediate stages in the

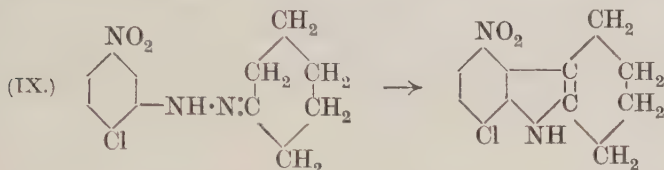
² Compare J. Kenner and E. Witham, *T.*, 1921, **119**, 1452.

³ R. Stollé and E. Knebel, *Ber.*, 1921, **54**, [B], 1213; *A.*, i, 578; H. Staudinger, E. Schlenker, and H. Goldstein, *Helv. Chim. Acta*, 1921, **4**, 434; *A.*, i, 432.

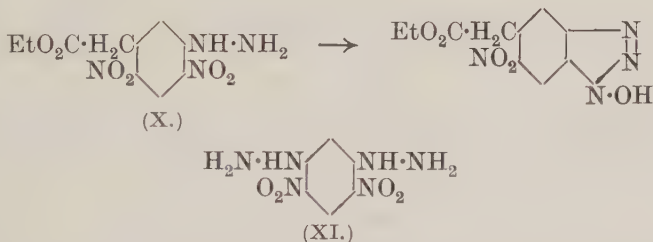
⁴ K. von Auwers, *Annalen*, 1920, **421**, 1; *A.*, 1920, i, 866.

⁵ H. Staudinger, E. Schlenker, and H. Goldstein, *loc. cit.*

reaction. Again, tetrahydrocarbazole is best prepared by an application of the well-known indole synthesis, consisting in boiling *cyclohexanonephenylhydrazone* with glacial acetic acid, and this reaction has been successfully extended to the 2-chloro-5-nitrophenylhydrazone (IX):⁶



Another factor which appears to affect the formation of rings on two sides of a central benzene nucleus is some disinclination to their production in straight alignment, as typified by anthracene. The illustration, supplied in last year's Report,⁷ of the formation of an acrylic acid rather than a coumarin, from 5-hydroxycoumarone-4-aldehyde by condensation with acetic anhydride and sodium acetate, has been confirmed.⁸ Further, whereas ethyl 2:4-dinitro-5-hydrazinophenylacetate (X) is easily converted by alkali into an azimino-compound, according to the reaction usually exhibited by *o*-nitrophenylhydrazines,



4:6-dinitro-1:3-dihydrazinobenzene (XI) is decomposed by alkali with evolution of gas.⁹ That the resistance to the formation of a ring system of the anthracene type is not, however, always invincible, is shown by an investigation,¹⁰ which has also cleared up the disputed question as to the mode of coupling of *m*-phenylenediamines. Thus, from benzeneazo-*m*-phenylenediamine (XII), a triazole derivative (XIII) is obtained by oxidation with ammoniacal copper

⁶ W. H. Perkin, jun., and S. G. P. Plant, *T.*, 1921, **119**, 1825; compare Drechsel, *J. pr. Chem.*, 1888, [ii], **38**, 65; Baeyer, *Ber.*, 1889, **22**, 2185; *Annalen*, 1894, **278**, 105; *A.*, 1888, 1276; 1889, 1162; 1894, 174.

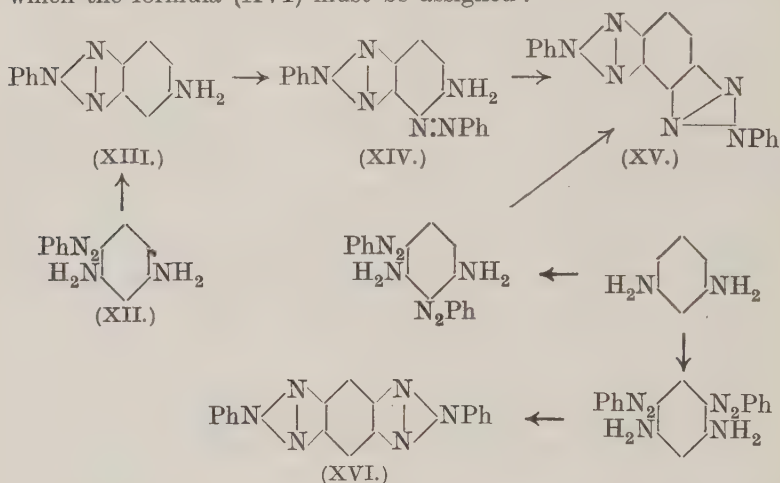
⁷ P. 102.

⁸ P. Karrer, A. Rüdinger, A. Glattfelder, and L. Waitz, *Helv. Chim. Acta*, 1921, **4**, 718; *A.*, i, 800.

⁹ W. Borsche, *Ber.*, 1921, **54**, [B], 669; *A.*, i, 461.

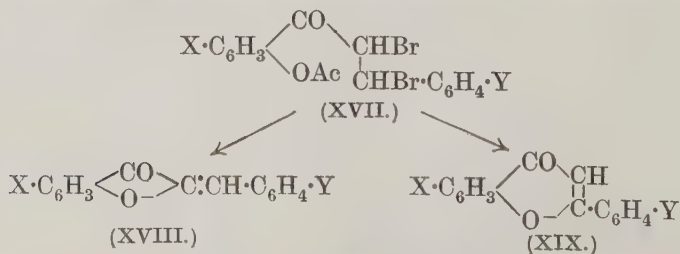
¹⁰ M. P. Schmidt and A. Hagenböcker, *ibid.*, 2191; *A.*, i, 897; Kalle and Co., *Patentanmeldung*, K 60493, iv, 12 pp.

sulphate solution. Since only those substitution derivatives of this compound, as of β -naphthylamine, will couple further which have a free 4-position, benzeneazo-5-amino-2-phenyl-2 : 1 : 3-benzotriazole has the formula (XIV), and so furnishes a bistriazole of the constitution (XV). This product is also obtainable from the compound contained in the filtrate from the dye prepared by coupling *m*-phenylenediamine with two molecules of diazotised aniline. The dye itself may be converted into an isomeric compound, to which the formula (XVI) must be assigned :



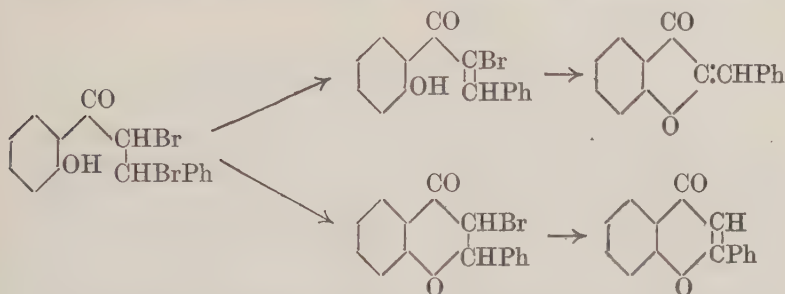
It therefore follows that coupling with *m*-phenylenediamine occurs in both the possible ways, a point in noteworthy contrast with the behaviour of the triazole derivative.

Further work has emphasised the intricacy of the conditions governing the formation of cyclic compounds from derivatives of *o*-hydroxyphenyl vinyl ketone.¹¹ Thus, it has long been known that the bromides of *o*-acetoxyphenyl styryl ketones (XVII) are converted by treatment with alkali in some cases into coumaranones (XVIII), in others into flavones (XIX), according to the nature and position of the substituents in the two nuclei :

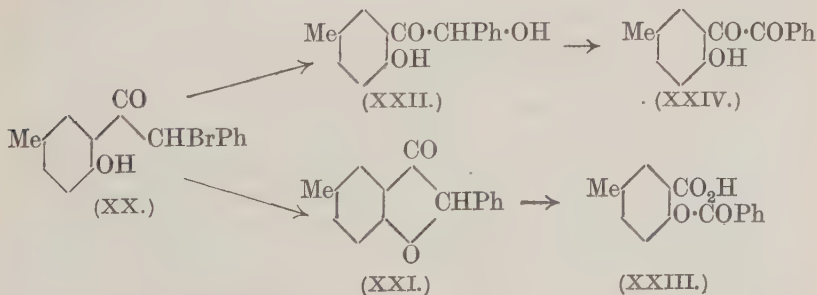


¹¹ Compare *Ann. Reports*, 1920, 17, 101.

In explanation, it has been supposed that the former change occurs when the difficulty of hydrolysis permits the prior formation of the bromostyryl ketone, whilst the latter occurs when the acetyl group is easily hydrolysed.¹² This is, however, not the case, since the dibromides of *o*-hydroxyphenyl styryl ketones may be converted into coumaranones by the addition of hot aqueous sodium hydroxide to their hot alcoholic solution, whilst at the ordinary temperature they yield flavones. The result appears to be due to the simultaneous operation of two parallel reactions, the relative velocities of which are determined partly by external conditions, partly by the nature of the substituents in the benzene nuclei :



The especial instability of the five-membered ring in the 1-alkylcoumaranones is apparently even more pronounced in the 1-phenyl derivatives.¹³ Thus, the action of sodium hydroxide on α -bromo-2-hydroxy-5-methyldeoxybenzoin (XX) should, according to the precedent of compounds containing an alkyl in place of a phenyl group in the side chain, give rise to 1-phenyl-4-methylcoumaranone (XXI).



The product, however, after prolonged exposure to the atmosphere consists chiefly of 2-hydroxy-5-methylbenzil (XXIV), with a small

¹² Kostanecki and Tambor, *Ber.*, 1899, **32**, 2268; *A.*, 1899, i, 891.

¹³ K. von Auwers and L. Anschütz, *ibid.*, 1921, **54**, [B], 1543; *A.*, i, 682; compare *Ann. Reports*, 1920, **17**, 100.

amount of 4-benzoyloxy-*m*-toluic acid (XXIII), which result from oxidation of the intermediate deoxybenzoin (XXII) and coumaranone respectively.¹⁴ It may be noted, however, that the methyl group probably contributes to the results, since the stability of coumaranones is diminished by the presence of such groups in the ortho- or para-position to the oxygen atom.

The results of the action of phenylhydrazine on the phenyl vinyl ketones are also interesting.¹⁵ It is quite in accordance with anticipation that the formation of pyrazolines should become progressively more difficult as the ketone (XXV) is modified by the introduction of methyl groups in place of the hydrogen atoms of its methylene group :



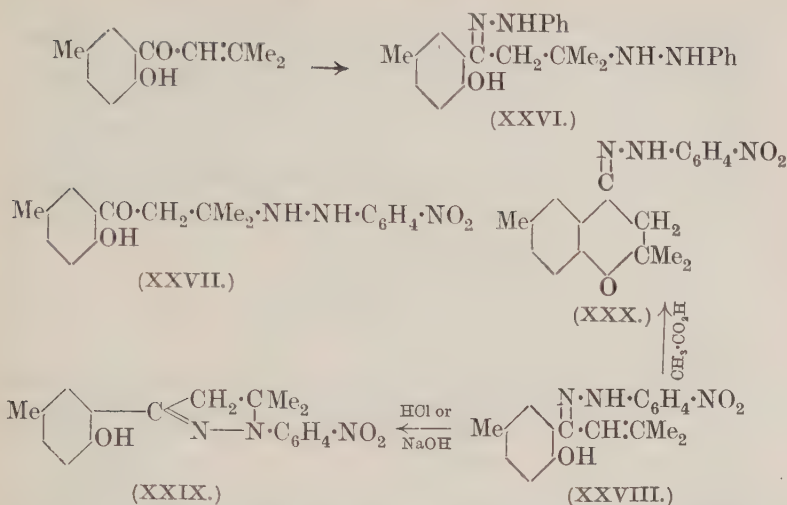
It may also be argued that the formation of a hydrazino-hydrazone (XXVI), with an azo-compound derived from it by oxidation, from 4-hydroxy-*m*-tolyl *isobutenyl* ketone¹⁶ is due to the effect of the ortho-hydroxyl group in so diminishing the rate of hydrazone formation that addition occurs at the double bond with a relatively much greater velocity. Indeed, if *p*-nitrophenylhydrazine be employed, the hydrazino-compound (XXVII) represents the final product, since a hydrazone cannot be prepared from it. Further, it is not surprising that the normal hydrazone (XXVIII) can be obtained by the use of the hydrazine hydrochloride, since this would obviously have little tendency to react additively at the ethylene linking. But it is remarkable that the hydrazone (XXVIII) is converted into a pyrazoline (XXIX) by means of sodium hydroxide (or hydrochloric acid), since alkali causes the rearrangement of the original ketone into a chromanone.

Again, the *p*-nitrophenylhydrazone (XXX) of this chromanone is obtained by the use of hot glacial acetic acid—a reagent which, in the case of the compound (XXV), facilitates pyrazoline formation. The fineness of the balance between the tendencies to chromanone and pyrazoline formation will be apparent from the fact that from five experiments carried out with glacial acetic acid the chromanone was obtained in three, the pyrazoline in two, cases. The easy formation of a hydrazone from the azo-compound corresponding with the non-reactive hydrazino-compound (XXVII) is also noteworthy.

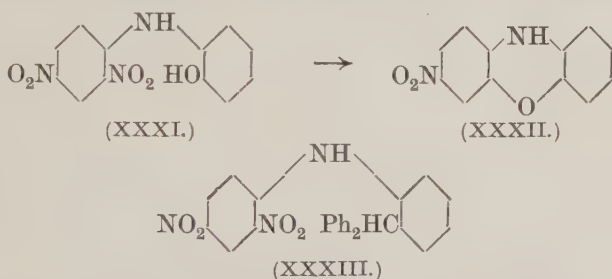
¹⁴ K. von Auwers, *Ber.*, 1920, **53**, [B], 2271; *A.*, i, 118.

¹⁵ K. von Auwers and H. Voss, *ibid.*, 1909, **42**, 4411; *A.*, 1910, i, 70; E. P. Kohler, *Amer. Chem. J.*, 1909, **42**, 775; *A.*, 1909, i, 938.

¹⁶ K. von Auwers and E. Lämmerhirt, *Ber.*, 1921, **54**, [B], 1000; *A.*, i, 464.



The syntheses of azines from picryl chloride by condensation with *o*-amino-phenols or -thiophenols, or *o*-phenylenediamines, and subsequent treatment with alkali, are well known, and can be applied to the case of 1-chloro-2 : 6-dinitrobenzene.¹⁷ But 2 : 4-dinitro-2'-hydroxydiphenylamine (XXXI) is converted into an oxazine (XXXII) only with much difficulty,¹⁸



whilst 2 : 4-dinitro-2'-benzhydryldiphenylamine (XXXIII) could not be converted into a nitrodiphenylcarbazine,¹⁹ and a nitrophenyldihydrophenazine could not be obtained from 2 : 4-dinitro-2'-anilindiphenylamine.²⁰ Yet the 2 : 6-, and, of course, the 2 : 4 : 6-trinitro-analogues are in each case amenable to condensation. Here again, therefore, the position of a substituent is a considerable factor in determining the result.

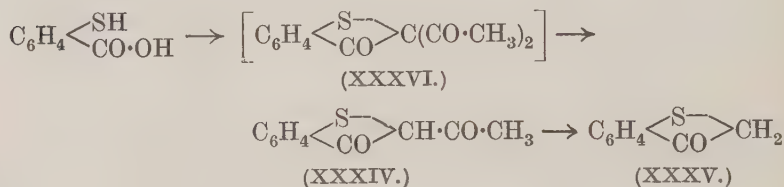
¹⁷ F. Ullmann and E. Kuhn, *Annalen*, 1909, **366**, 79; *A.*, 1909, i, 473.

¹⁸ F. Kehrman and (Miss) M. Ramm, *Ber.*, 1920, **53**, [B], 2265; *A.*, i, 128.

¹⁹ F. Kehrman, (Miss) M. Ramm, and Ch. Schmajewski, *Helv. Chim. Acta*, 1921, **4**, 538; *A.*, i, 600.

²⁰ K. Kehrman and J. Effront, *ibid.*, 517; *A.*, i, 601.

The operation of yet another factor on the stability of cyclic compounds seems to be distinguishable in the course of the condensation of 2-thiolbenzoic acid with compounds containing a reactive methylene group in presence of sulphuric acid. For example, the usual product from acetylacetone is 3-oxy(1-)thionaphthen (XXXV). Its 2-acetyl derivative (XXXIV) is obtained only under mild conditions of reaction, whilst the 2:2-diacetyl derivative (XXXVI), of which the initial formation is to be presumed, cannot be isolated:²¹



Since 2-acetyl-3-oxy(1-)thionaphthen is a tautomeric substance, the decomposition of the diacetyl derivative would appear to be due to its tendency to acquire a tautomeric hydrogen atom.²² Further, since the alcoholic solution of the monoacetyl derivative is coloured green by ferric chloride, the compound evidently exists to some extent in the enolic form, which, in the case of ethyl acetoacetate itself, is known easily to undergo acid hydrolysis. The 3-oxythionaphthens are intermediate in their chemical properties between the coumaranones and the hydrindones.²³

Ring Transformations.

A number of instances have been recorded in recent years of the transformation of the five-membered ring of isatin into a six-membered ring. In addition to those already noticed in these Reports,²⁴ reference may be made to the formation of cinchonic acids by condensation of isatin with compounds, such as phenylacetic and malonic acids,²⁵ which contain a reactive methylene group. The products (XXXVII) and (XXXVIII) are obtained in the cases mentioned. Since the acid (XXXIX) is obtained from *N*-methyl-

²¹ S. Smiles and E. W. McClelland, *T.*, 1921, **119**, 1810; compare A. M. Hutchison and S. Smiles, *T.*, 1912, **101**, 570.

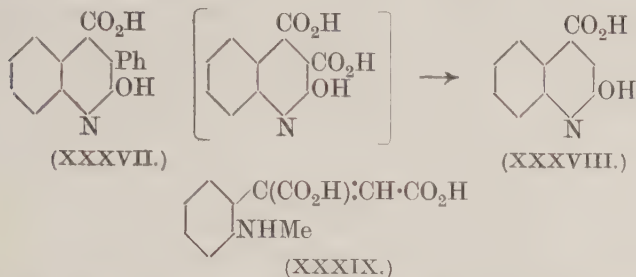
²² Compare F. B. Thole and J. F. Thorpe, *T.*, 1911, **99**, 2183.

²³ K. von Auwers and W. Thies, *Ber.*, 1921, **54**, [B], 2285; *A.*, i, 120.

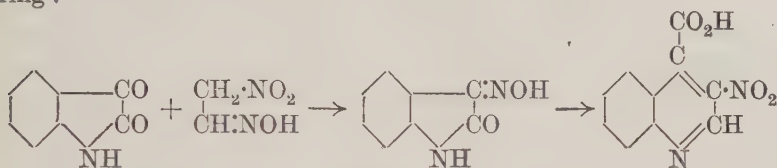
²⁴ *Ann. Reports*, 1919, **16**, 112; also G. Heller and P. Jacobsohn, *Ber.*, 1921, **54**, [B], 1107; *A.*, i, 440.

²⁵ W. Borsche and W. Jacobs, *ibid.*, 1914, **47**, 354; W. Borsche and W. Sander, *ibid.*, 2815; W. Borsche and R. Meyer, *ibid.*, 1921, **54**, [B], 2841; *A.*, 1914, i, 322; 1915, i, 299; 1922, i, 53.

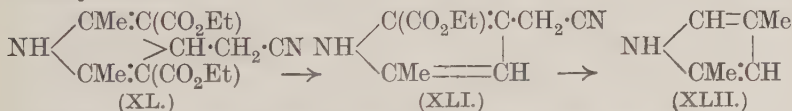
isatin, the formation of an analogous intermediate product from isatin is assumed :



The conversion of isatin into its β -oxime and 3-nitroquinoline-carboxylic acid by condensation with methazonic acid in presence of alkali²⁶ also involves at some stage the opening of the indole ring :



The reverse process—transformation of a pyridine into a pyrrole ring—has now been observed for the first time. Ethyl 2 : 6-dimethyl-4-cyanomethyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate (XL) is converted into ethyl 5-methyl-3-cyanomethylpyrrole-2-carboxylate (XLI) under the influence of boiling alcoholic potassium hydroxide :



The reaction is dependent on the presence of the cyanogen group, since ethyl 2 : 4 : 6-trimethyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate does not undergo a similar change. The constitution of the product (XLI) is established by its eventual conversion into 2 : 4-dimethylpyrrole (XLII),²⁷ but it will be noticed that this is not conclusive in respect of the carbethoxy-group.

Structural Isomerism.

A polemical discussion²⁸ has arisen in regard to the existence

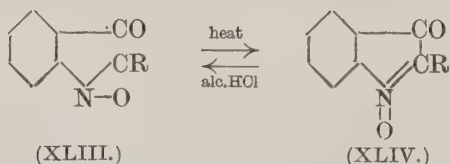
²⁶ B.A.S.F., D.R.-P. 335197; *A.*, i, 517.

²⁷ E. Benary, *Ber.*, 1920, **53**, [B], 2218; *A.*, i, 127.

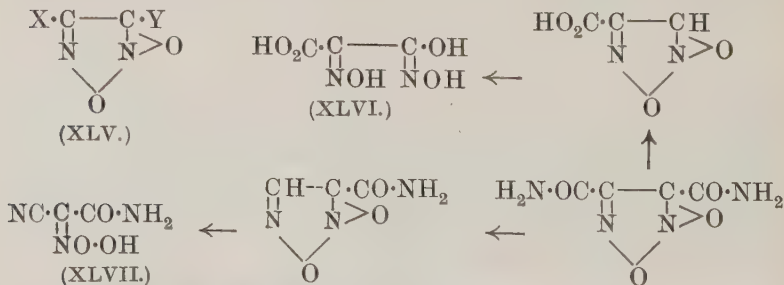
²⁸ A. Hantzsch, *ibid.*, 1921, **54**, [B], 1221, 1257; G. Heller, *ibid.*, 2214; *A.*, i, 597, 598.

of the various alleged isomerides of isatin.²⁹ As the matter is still in debate a fuller account is postponed, but an interesting point has emerged which bears on Hartley's classical measurements of the absorption spectrum of *O*-methylisatin. It was overlooked that this compound rapidly isomerises in solution. This was perhaps fortunate, since the close resemblance of the absorption of this compound in freshly prepared solutions to those of isatin and its *N*-methyl derivative might have delayed recognition of a method which has since proved of such value in connexion with the study of tautomeric compounds.

A further investigation of the *isoisatogens*, derived from the more highly coloured isatogens by treatment with alcoholic hydrogen chloride, has shown that they have the molecular weight demanded by the formula (XLIII) originally proposed for them,³⁰ lack the oxidising properties of the isatogens, and are not phenolic, but exhibit ketonic properties. Their reconversion into the isatogens (XLIV), by heating them alone or in glacial acetic acid solution or, most effectively, with phenylcarbimide, also indicates the intimate relationship suggested by the formulæ : ³¹



The formula (XLV) for the furoxans has been defended³² on the ground that there is evidence of asymmetry in these compounds. Thus, the amide of furoxandicarboxylic acid is decomposed,



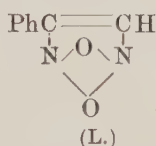
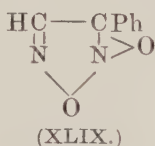
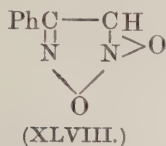
²⁹ G. Heller, *Ber.*, 1907, **40**, 1291; 1916, **49**, 2757; 1917, **50**, 1199; 1918, **51**, 180, 1270; 1919, **52**, 437; 1920, **53**, [B], 1545; *A.*, 1907, i, 442; 1917, i, 219, 708; 1918, i, 235; 1919, i, 36, 282; 1920, i, 766.

³⁰ Compare *Ann. Reports*, 1919, **15**, 109.

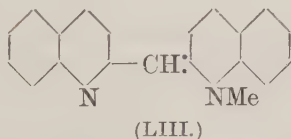
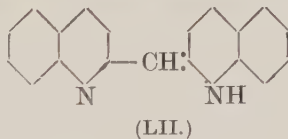
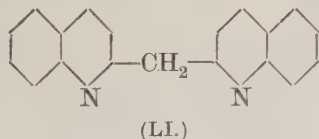
³¹ P. Ruggli and A. Bolliger, *Helv. Chim. Acta*, 1921, **4**, 626, 637; *A.*, i, 811, 812.

³² H. Wieland, *Annalen*, 1921, **424**, 107; *A.*, i, 605.

according to the conditions employed, into *isonitrosohydroxamic acid* (XLVI),³³ or into *fulminuric acid* (XLVII).³⁴ Although all the methods of formation of phenylfuroxan, as would be expected, yield the same product (XLVIII) rather than (XLIX), they, and also the action of nitrogen trioxide on phenylacetylene, first give rise to an unstable isomeride of phenylfuroxan, which passes into the known derivative, and which may possibly correspond with the formula (L).³⁵



An interesting form of desmotropy has been observed with both di- and tri-2-quinolylmethanes. These compounds, which are prepared by the interaction of suitable quantities of quinaldine and 2-chloroquinoline, each exist in two interconvertible modifications. Thus, di-2-quinolylmethane, when first prepared, is a mixture of the colourless compound (LI) with a small amount of a red isomeride (LII), which is decolorised by bromine and in alcoholic solution is slowly converted into the colourless form, more rapidly in presence of alkali. The same two series of salts—coloured monoacidic and colourless diacidic—are obtainable from each. *N*-Methyl-2-quinolylenequinaldine (LIII), prepared by methylation with methyl iodide or sulphate, is also red and stable.³⁶



A reference to isomerism among thiophen derivatives will be found on p. 125.

³³ H. Wieland, *Annalen*, 1909, **367**, 56; *A.*, 1909, i, 609.

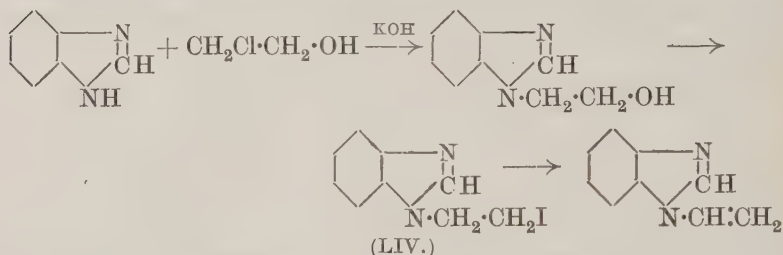
³⁴ C. Ulpiani, *Gazzetta*, 1905, **35**, ii, 7; *A.*, 1905, i, 750.

³⁵ Compare A. G. Green and F. M. Rowe, *T.*, 1912, **101**, 2452; 1914, **105**, 897, 2023.

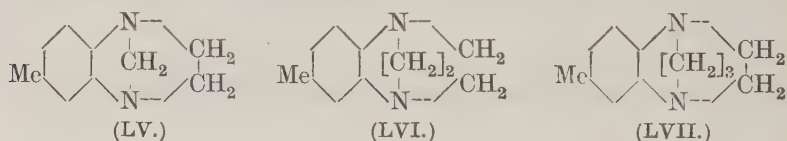
³⁶ G. Scheibe and E. Rossner, *Ber.*, 1920, **53**, [B], 2064; G. Scheibe, *ibid.*, 1921, **54**, [B], 786; *A.*, i, 62, 451.

Stereoisomerism.

Further attempts have been recorded to prepare tervalent nitrogen compounds, the configuration of which would be likely to prove sufficiently stable to permit their resolution. One investigation,³⁷ in which the following series of reactions was attempted,

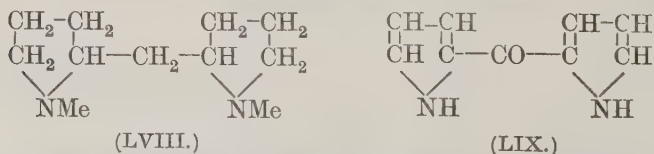


was unsuccessful because, in place of the desired 1-β-iodoethyl-benziminazole (LIV), a polymeride, resulting from intermolecular quaternary ammonium iodide formation, was obtained. The statement that a side-chain could not be introduced into tetrahydroquinoxaline is at variance with an account³⁸ of the preparation of 1:4-*endo*-methylene-, -ethylene-, and -trimethylene-6-methyltetrahydroquinoxalines (LV, LVI, and LVII) by treatment



of tetrahydroquinoxaline with methylene iodide or formaldehyde, ethylene dibromide, and trimethylene dibromide respectively.

Experiments on the synthesis of di-*N*-methyldi-α-pyrrolidylmethane (LVIII), obtained as a degradation product of cusk-hygrine,³⁹ have yielded notable results.⁴⁰ Di-α-pyrrol ketone (LIX) is best prepared by the action of carbonyl chloride on magnesium



³⁷ J. Meisenheimer and B. Wieger, *J. pr. Chem.*, 1921, [ii], **102**, 45; *A.*, i, 739.

³⁸ T. S. Moore and (Miss) I. Doubleday, *T.*, 1921, **119**, 1170.

³⁹ Compare *Ann. Reports*, 1920, **17**, 126.

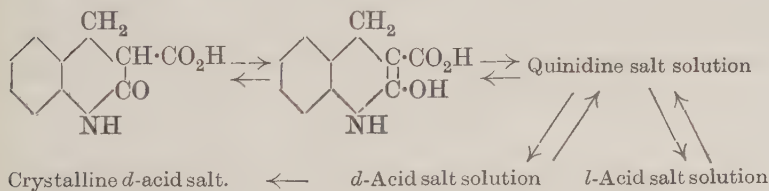
⁴⁰ K. Hess and F. Anselm, *Ber.*, 1921, **54**, [B], 2310; *A.*, i, 881.

pyrrol bromide or, less satisfactorily, potassium pyrrole,⁴¹ and has also been obtained from α -pyrrolyl chloride and magnesium pyrrol bromide.⁴² By catalytic reduction, di- α -pyrrolidylmethane is obtained, and this is converted into the desired compound by treatment with formaldehyde.

Both these pyrrolidine derivatives, however, are mixtures of stereoisomerides. The *N*-methyl compound furnishes three distinct methiodides, which differ from the two now found to be obtainable from the degradation product of cuskhygrine. It is tentatively suggested that the existence of these five isomerides is another illustration of stereoisomerism connected with the two nitrogen atoms, which, in conjunction with the two asymmetric carbon atoms, would result in the existence of two meso- and four racemic compounds. If this be so, it is interesting that the products of natural synthesis should differ in configuration from those obtained in the laboratory.

Asymmetric Rearrangement.

An automatic resolution of the quinidine salt of *r*-hydrocarbostyryl-3-carboxylic acid (LX) occurs when this is prepared in methyl alcoholic solution from its components, since the sole product, which is obtained quantitatively, is that derived from the *d*-acid. The result is due to the enolisation of the acid and the relatively sparing solubility of the salt of the *d*-acid :



The result only differs from an asymmetric synthesis in that throughout no change of molecular weight is involved, and is therefore termed an "asymmetric rearrangement."⁴³ Confirmation of this explanation is derived from the gradual racemisation of the free active acid, which commences immediately the acid is dissolved. 2-*o*-Carboxybenzylhydrindone (LXI) undergoes a similar resolution through its brucine salt.⁴⁴ The formation of an inactive sulphone from the optically active forms of α -thiodipropionic acid⁴⁵ (LXII) is possibly due to similar causes.

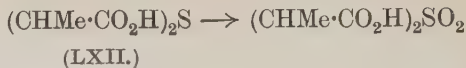
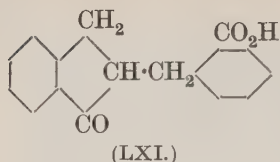
⁴¹ G. Ciamician and P. Magnaghi, *Ber.*, 1885, **18**, 419; *A.*, 1885, 809.

⁴² B. Oddo, *Gazzetta*, 1920, **50**, ii, 258; *A.*, i, 129.

⁴³ H. Leuchs, *Ber.*, 1921, **54**, [B], 830; *A.*, i, 442.

⁴⁴ H. Leuchs and J. Wutke, *ibid.*, 1913, **46**, 2425; *A.*, 1913, i, 974.

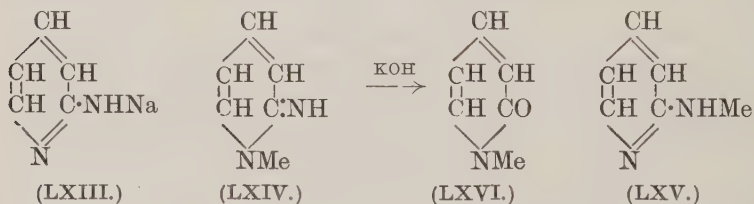
⁴⁵ J. M. Lovén and R. Ahlberg, *ibid.*, 1921, **54**, [B], 227; *A.*, i, 223.



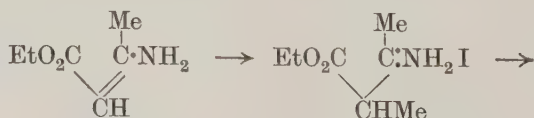
Alkylation.

Alkylation represents one of the most valued and general methods of investigation at the disposal of the organic chemist, and corresponding importance attaches to inquiries as to the variation to be obtained in the results by modification of the experimental conditions.

By the action of methyl iodide on either 2-aminopyridine or its sodium derivative (LXIII), two methyl derivatives are obtained. 1-Methyl-2-pyridoneimide (LXIV) is the chief product in the former case, whilst 2-methylaminopyridine (LXV) predominates in the latter :



The structure of the imino-derivative is proved by its hydrolysis with alkali to ammonia and 1-methyl-2-pyridone (LXVI).⁴⁶ Its stability towards dilute acids differentiates it from ordinary ketimines, but it may be observed that the same property is exhibited by the analogously constituted amidines.⁴⁷ Interesting as these results are, it may be doubted whether they justify the idea that they are evidence of "the tautomerism of α -aminopyridine," and the same applies to other cases of a similar kind.⁴⁸ Thus, the formation of the ketimine is possibly the outcome of reactions closely resembling those by which ethyl α -acetylbutyrate is obtained from ethyl β -aminocrotonate :⁴⁹

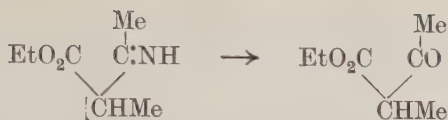


⁴⁶ A. E. Tschitschibabin, R. A. Konowalowa, and A. A. Konowalowa, *Ber.*, 1921, **54**, [B], 814; *A.*, i, 450.

⁴⁷ Compare, for example, H. von Pechmann, *ibid.*, 1895, **28**, 2368; *A.*, 1896, i, 31.

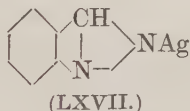
⁴⁸ A. E. Tschitschibabin, *ibid.*, 1921, **54**, [B], 822; *A.*, i, 451.

⁴⁹ R. Robinson, *T.*, 1916, **109**, 1039.



The analogy between the behaviour of the two amino-compounds is not, however, complete, since the crotonate and its sodium derivative do not furnish a mixture of products on alkylation, and ethyl β -amino- α -methylcrotonate, derived from the sodium derivative, does not correspond with the main product from 2-pyridyl-sodamide. But it must also be remembered that the tertiary nitrogen atom of 2-aminopyridine, unlike the methine carbon atom in ethyl β -aminocrotonate, shares with the amino-group the capacity for combination with the halogen atom of the alkyl iodide.

The danger of basing conclusions solely on the results of alkylation is strikingly illustrated by experiments in the indazole series.⁵⁰ The following may serve as illustrations of the variety of results obtained. From silver indazole (LXVII) and suitable alkyl iodides at the ordinary temperature, 2-methyl, 1-benzyl, and 1-allyl derivatives were obtained, but increasing amounts of the 1-methyl isomeride resulted as the temperature of reaction was raised. The direct interaction of indazole with alkyl iodides at 100° gave rise to mixtures, in which the 2-derivatives predominated. By the use of one sample of benzyl chloride at 140°, 1-benzylindazole was produced, whilst another sample consistently yielded the 2-derivative. Alkylation in presence of boiling alcoholic sodium hydroxide usually furnished approximately equal amounts of the 1- and 2-isomerides.



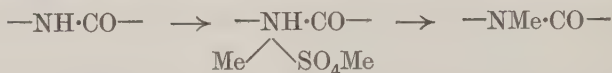
A detailed study⁵¹ of the methylation of uric acid shows that this also is a somewhat complicated process. Conductivity measurements of the various methyluric acids show that the acidity of the hydrogen atoms in positions 3, 9, 1, and 7 diminishes in the order given, the last two being so feebly acid that uric acid is dibasic. Alkylation of the dry lead or potassium salts with alkyl iodides corresponds with that of ethyl acetoacetate, and results in the formation first of 3-, then of 9-methyl derivatives, and the same applies to alkyl derivatives in which these positions are free:



⁵⁰ K. von Auwers, *Ber.*, 1919, **52**, 1330; K. von Auwers and R. Dereser, *ibid.*, 1340; K. von Auwers and W. Schaich, *ibid.*, 1921, **54**, [B], 1738; *A.*, 1919, **i**, 455, 456; 1921, **i**, 806.

⁵¹ H. Biltz and (Miss) L. Herrmann, *ibid.*, 1921, **54**, [B], 1676; *A.*, **i**, 691.

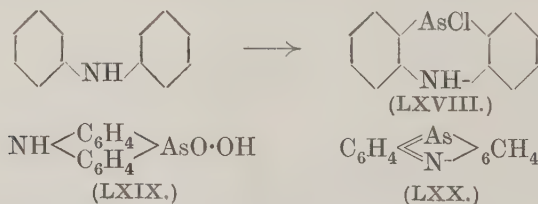
By the use of methyl sulphate and alkaline solutions, however, the least acidic hydrogen atoms are first replaced. Thus the respective products from 3:7-, 7:9-, and 3:9-dimethyluric acids are 1:3:7-, 1:7:9-, and equal proportions of 1:3:9- and 3:7:9-trimethyluric acids. Probably quaternary methyl metho-sulphates are first produced, and this occurs by preference at the most basic (least acidic) nitrogen atom of the uric acid molecule :



But this explanation does not seem to meet all the facts, since, by treatment of uric acid with methyl sulphate, a considerable proportion of 1:3-dimethyluric acid is produced. It would therefore appear that other factors are in operation, as, indeed, is recognised to be the case when methyl iodide is used in place of the sulphate. The mode of action of formaldehyde appears to correspond with that of methyl sulphate. The use of diazo-methane⁵² yields noteworthy results. Although compounds in which the 3- and 9-positions are already alkylated do not react, substitution also occurs in the 1- and 7-positions when either of the former positions is free. Further, 8- and 2-alkoxy-derivatives are formed in certain cases, but only one such group is produced. Thus uric acid gives rise to 8-methoxy-2:6-dihydroxy-1:3:7-trimethylpurine, which changes at 200° into 1:3:7:9-tetramethyluric acid.

Heterocyclic Arsenic Compounds.

The arsenic analogues of phenyl-piperidine and -pyrrolidine were the only heterocyclic arsenic compounds known⁵³ until it was observed that phenarsazine chloride (LXVIII) is readily obtained by boiling a mixture of arsenious chloride with diphenylamine :⁵⁴



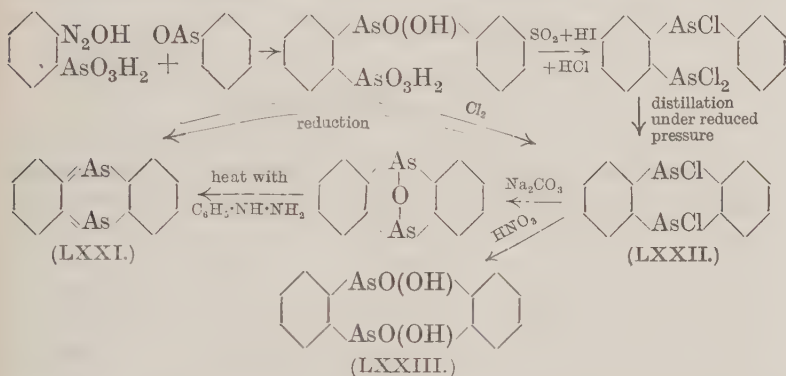
The product resembles diphenylarsenious chloride both in its sternutatory and in its chemical actions. The corresponding oxide (but not the hydroxide), methyl ether, acetate, and sulphide

⁵² H. Biltz and F. Max, *Ber.*, 1920, **53**, [B], 2327; *A.*, i, 131.

⁵³ Compare *Ann. Reports*, 1916, **13**, 131.

⁵⁴ D.R.-P. 281049 (1915).

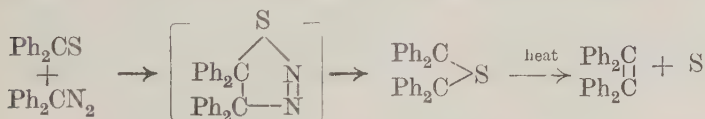
are easily obtained and reconverted into the chloride, whilst phenarsazinic acid (LXIX) is obtained by oxidation. Phenarsazine (LXX), best obtained by heating phenarsazine methyl ether, is an orange-yellow compound, characterised by the special avidity, reminiscent of the ketens, with which it is reconverted into phenarsazine derivatives by direct combination with suitable reagents.⁵⁵ Further, arsanthrene (LXXI) has been prepared⁵⁶ by the reactions indicated in the following scheme :



The orange-yellow product, or its chloride (LXXII), is oxidised by nitric acid to arsanthrenic acid (LXXIII).⁵⁵

Some Heterocyclic Sulphur Compounds.

Interesting results have been obtained by the action of various thio-derivatives on diazo-compounds. Thus, diphenyldiazomethane and thiobenzophenone yield tetraphenylethylene sulphide,⁵⁷ which could not be oxidised to the corresponding sulphone,⁵⁸ and is decomposed by heat into tetraphenylethylene and sulphur :



From thiocarbonyl chloride and diphenyldiazomethane, *as*-dichlorodiphenylethylene sulphide (LXXIV) is first obtained, but gradually

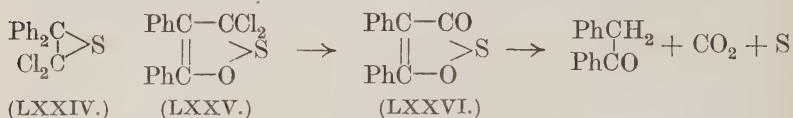
⁵⁵ H. Wieland and W. Rheinheimer, *Annalen*, 1921, **423**, 1; *A.*, i, 371.

⁵⁶ L. Kalb, *ibid.*, 39; *A.*, i, 375.

⁵⁷ H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, 1920, **3**, 833; *A.*, i, 43.

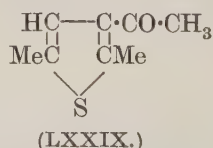
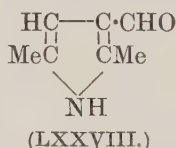
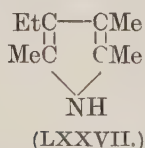
⁵⁸ Compare H. Staudinger and F. Pfenninger, *Ber.*, 1916, **49**, 1941; *A.*, 1916, i, 852.

changes into *as*-dichlorodiphenylethylene and sulphur.⁵⁹ Its chlorine atoms are not reactive, but the product (LXXV) obtained from benzoylphenyldiazomethane and thiocarbonyl chloride is decomposed by the moisture of the atmosphere into the compound (LXXVI), from which deoxybenzoin and sulphur are produced by the action of alkali :



Five-membered Heterocyclic Structures.

It has long been known that the entrance of substituents into the carbon system of the pyrrole ring, whether directly or in consequence of molecular rearrangement of *N*-substituted derivatives, normally occurs in the 2-position. Evidence is, however, accumulating that 3-derivatives may also be formed if the 2-position is not free. Thus, by the action of sodium ethoxide on 2 : 3 : 5-trimethylpyrrole at 200°, its 4-ethyl derivative (phyllopyrrole) (LXXVII), was synthesised.⁶⁰ Again, 1-formyl-2 : 5-dimethylpyrrole suffers rearrangement at 200° in presence of zinc chloride into 3-aldehydo-2 : 5-dimethylpyrrole (LXXVIII) :



Similarly, in the thiophen series, 2-thienyl ketones are formed by the action of acid anhydrides on thiophen.⁶¹ But, from 2 : 5-dimethylthiophen 2 : 5-dimethyl-3-thienyl methyl ketone (LXXIX) is obtained, although the reaction proceeds less easily.⁶² Further, it had been hoped that the formation of thienylmercurichlorides from thiophens⁶³ by the action of mercuric chloride would afford a means of distinguishing 1- from 2-derivatives. This is, however, not the case, since the additive compound (LXXX) has been obtained from 2 : 5-dimethylthiophen, corresponding with that formed by the 2 : 4-isomeride (LXXXI) : ⁶⁴

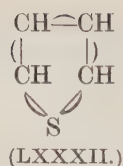
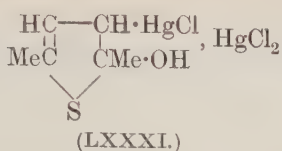
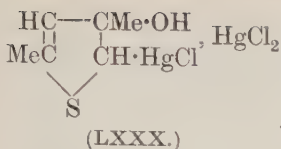
⁵⁹ H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, 1920, **3**, 840; *A.*, i, 43.

⁶⁰ H. Fischer and E. Bartholomäus, *Ber.*, 1912, **45**, 466; *A.*, 1912, i, 297.
⁶¹ *Ann. Reports*, 1917, **14**, 124.

⁶² W. Steinkopf and J. Schubert, *Annalen*, 1921, **424**, 1; *A.*, i, 579.

⁶³ *Ann. Reports*, 1917, **14**, 123.

⁶⁴ W. Steinkopf, *Annalen*, 1921, **424**, 23; *A.*, i, 630.



These compounds also have the interest that they render probable the formation of such compounds in general as a preliminary to the mercurichlorides proper. These, with the mercurithiocyanates obtained from them by double decomposition with sodium thiocyanate, can be used to characterise the alkyl and aryl thiophens. By this method, an interesting case of isomerism has been discovered. 2 : 5-Diphenylthiophen, m. p. 152°, from diphenacetyl and phosphorus pentasulphide,⁶⁵ gives the same mercury derivatives as the isomeric product, m. p. 119°, obtained from anhydrotriacetophenone disulphide.⁶⁶ The result recalls the existence of two forms of dinitrothiophen, of which one is convertible into the other.⁶⁷

Thiophen may be mono- or di-halogenated by suitable treatment with aceto-chloro- or -bromo-amide.⁶⁸ Although this reaction indicates a certain degree of unsaturation,⁶⁹ it is suggested that the formula (LXXXII) offers the best expression of the properties of thiophen. No experiments are described on the attempted halogenation of 2 : 5-substituted thiophens by this method.

Recognition of the fact that the therapeutic value of ichthyol oils is due to the presence of alkylthiophens⁷⁰ has stimulated interest in these compounds. The propyl and isopropyl derivatives have been prepared by the classical methods,⁷¹ but these and methods depending on the action of sulphur on olefines⁷² or of iron pyrites on butadienes⁷³ are inferior to that which consists in the reduction of the corresponding ketones by Clemmensen's method.⁷⁴

Hydrazine is not a suitable reagent for the reduction of indigotin to indigo-white, since it has no effect by itself, whilst in presence of alkali reduction occurs, but the solution gradually loses its dyeing

⁶⁵ S. Kapf and C. Paal, *Ber.*, 1888, **21**, 3058; *A.*, 1888, 839.

⁶⁶ E. Baumann and E. Fromm, *ibid.*, 1897, **30**, 117; *A.*, 1897, i, 191.

⁶⁷ V. Meyer, "Die Thiophengruppe," p. 98.

⁶⁸ W. Steinkopf and A. Otto, *Annalen*, 1921, **424**, 61; *A.*, i, 579.

⁶⁹ Compare A. Wohl, *Ber.*, 1921, **54**, [B], 476; *A.*, i, 317.

⁷⁰ H. Scheibler, *Arch. Pharm.*, 1920, **258**, 84.

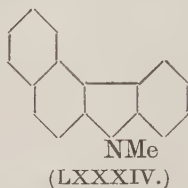
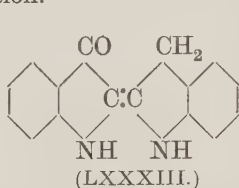
⁷¹ H. Scheibler and M. Schmidt, *Ber.*, 1921, **54**, [B], 139; *A.*, i, 191.

⁷² E. Baumann and E. Fromm, *ibid.*, 1895, **28**, 891; *A.*, 1895, i, 337.

⁷³ W. Steinkopf, *Annalen*, 1914, **403**, 11; *A.*, 1914, i, 425.

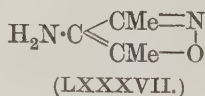
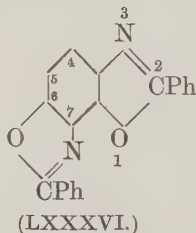
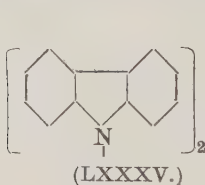
⁷⁴ W. Steinkopf and J. Schubert, *loc. cit.*

properties. If air be then drawn through the solution, a yellow precipitate will separate, to which the constitution (LXXXIII) is attributed. "Thioindigo" under similar conditions is converted into a leuco-compound, from which it is regenerated by the action of air.⁷⁵ The colour of indigotin and its derivatives has been discussed from the points of view both of its origin,⁷⁶ and of its relation to constitution.⁷⁷



The formation of *N*-methylnaphthaphenocarbazole (LXXXIV) by the action of *as*-phenylmethylhydrazine on 2-hydroxy-3-naphthoic acid in presence of sodium hydrogen sulphite⁷⁸ is important in that it confirms the view that the Bucherer-Lepetit reaction proceeds by formation of a bisulphite additive compound of the ketonic form of naphthols rather than of a sodium naphthylsulphite by condensation of the naphthol with the bisulphite.

The oxidation of carbazole with potassium permanganate results in the formation of three products, of which two have been identified as dicarbazyls, although their precise constitution is at present indefinite.⁷⁹ By the use of silver oxide, two products are obtained, of which one appears to be *NN*-dicarbazyl (LXXXV), and is interesting because, although colourless, it gives rise to reddish-brown solutions with a blue fluorescence. The freezing points of these in benzene indicate a dissociation varying from 20—40 per cent. directly with the concentration, but the compound does not yield a peroxide or decolorise iodine solution.⁸⁰



⁷⁵ W. Borsche and R. Meyer, *Ber.*, 1921, **54**, [B], 2854; *A.*, 1922, i, 55.

⁷⁶ R. Robinson, *J. Soc. Dyers and Col.*, 1921, **37**, 77; *A.*, i, 452.

⁷⁷ J. Martinet, *Rev. Gén. Mat. Col.*, 1921, **25**, 17; *A.*, i, 273.

⁷⁸ P. Friedländer, *Ber.*, 1921, **54**, [B], 620; *A.*, i, 443.

⁷⁹ W. H. Perkin, jun., and S. H. Tucker, *T.*, 1921, **119**, 216.

⁸⁰ G. E. K. Branch and J. F. Smith, *J. Amer. Chem. Soc.*, 1920, **42**, 2405; *A.*, i, 56.

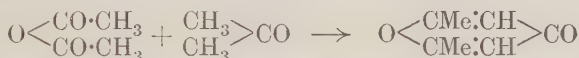
A study of the relationship between the constitution of benzoxazoles and their visible fluorescence ⁸¹ has shown that this occurs only when the 2-position is occupied by an aromatic group and a methyl or a salt-forming (for example, hydroxyl) group is present in the 6-position. Substitution in the 4-, 5-, or 7-position, however, may inhibit the fluorescence, as in the case of the compound (LXXXVI).

The property of diazotisability has been shown in recent years to be shared with aromatic amines by a number of heterocyclic compounds, to which 4-amino-3 : 5-dimethylisooxazole (LXXXVII) must now be added.⁸²

Two papers deal with the formation of double compounds of antipyrine with metallic salts.⁸³

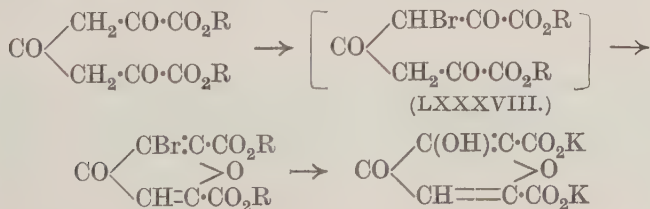
The Pyrone Group.

A straightforward synthesis of 2 : 6-dimethylpyrone consists in the gradual addition of sulphuric acid to an ice-cold mixture of acetone and acetic anhydride, although the yield amounts to only 4 per cent. : ⁸⁴



Similarly, by the use of methyl ethyl ketone, 2 : 3 : 6-trimethylpyrone is obtained.

A synthesis of meconic acid has been achieved ⁸⁵ by the bromination of ethyl acetonyldioxalate, followed by spontaneous dehydration of the primary product (LXXXVIII) into ethyl 3-bromo-chelidonate, from which potassium meconate was obtained by careful treatment with dilute potassium hydroxide solution.



⁸¹ F. Henrich, *Ber.*, 1921, **54**, [B], 2492; *A.*, i, 886.

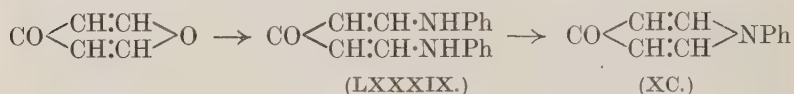
⁸² G. T. Morgan and H. Burgess, *T.*, 1921, **119**, 697.

⁸³ R. G. Fargher and H. King, *ibid.*, 292; E. Oliveri-Mandala, *Gazzetta*, 1921, **51**, i, 125; *A.*, i, 378.

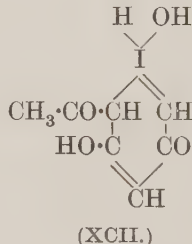
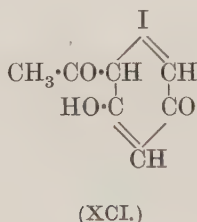
⁸⁴ E. Philippi and R. Seka, *Ber.*, 1921, **54**, [B], 1089; *A.*, i, 429; compare S. Skraup and J. Priglinger, *Monatsh.*, 1910, **31**, 250; *A.*, 1910, i, 578.

⁸⁵ H. Thoms and R. Pietrulla, *Ber. deut. Pharm. Ges.*, 1921, **31**, 4; *A.*, i, 264.

The result is in itself perhaps not decisive in favour of the γ -pyrone rather than of the open-chain formula⁸⁶ for meconic acid, since it is well known that the γ -pyrone ring is easily opened.⁸⁷ In illustration of this, it has been observed that γ -pyrone reacts with aniline acetate at the ordinary temperature, yielding bishydroxy-methyleneacetonedianilide (LXXXIX), from which *N*-phenyl- γ -pyridone (XC) is easily obtained by distillation or by treatment with acid or with sodium ethoxide.



Reference may also be made to an interesting compound indirectly derived from dimethylpyrone by its hydrolysis with barium hydroxide to the barium salt of diacetylacetone. By the action of iodine on an alcoholic suspension of this salt, a compound is obtained to which the formula (XCI) is assigned, and of which the acidic properties are attributed to its existence in aqueous solution in the form (XCII):⁸⁸



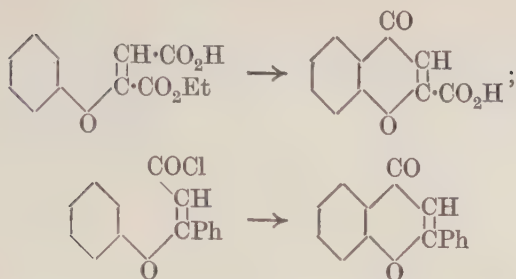
The method for the synthesis of chromones and flavones, which consists in the condensation of β -phenoxyfumaric acids by sulphuric acid and of β -phenoxybenzoyl chlorides by aluminium chloride,⁸⁹ has been applied to the preparation of derivatives containing chlorinated benzene nuclei, and also to the preparation of 6-benzene-azoflavone:

⁸⁶ W. Borsche, *Ber.*, 1916, **49**, 2538; *A.*, 1916, i, 117; *Ann. Reports*, 1917, **13**, 131.

⁸⁷ Compare, for example, R. Willstätter and R. Punmerer, *Ber.*, 1905, **38**, 1461; *A.*, 1905, i, 457.

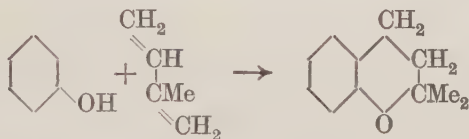
⁸⁸ J. N. Collie and (Miss) A. A. B. Reilly, *T.*, 1921, **119**, 1550; compare J. N. Collie and B. D. Steele, *T.*, 1900, **77**, 1116.

⁸⁹ S. Ruhemann, *Ber.*, 1913, **46**, 2188; *A.*, 1913, i, 891.



The yields of flavone derivatives are very satisfactory, but the chromones are less readily obtainable.⁹⁰ Other references to the synthesis of these compounds will be found in the section on ring formation.

2 : 2'-Dimethylchroman is formed by the direct combination of phenol with isoprene under conditions not definitely specified :⁹¹



The identity of the methylated reduction product of catechin tetramethyl ether⁹² is still under discussion. On the one hand,⁹³ it is claimed that no crystallographic difference exists between the product in question and synthetic 2 : 4 : 6 : 3' : 4'-pentamethoxy- $\alpha\gamma$ -diphenylpropane, that ordinary Gambir catechin is dextro-rotatory, acacatechin being a mixture of the lævo- with the racemic compound,⁹⁴ and hence that the reduction product about which discussion centres is also obtained from acacatechin tetramethyl ether. On the other hand,⁹⁵ the identity is claimed of acacatechin with a synthetic, and therefore inactive, 2 : 4 : 6 : 3' : 4'-penta-hydroxy-3-phenylchroman (XCIII), the tetramethyl ether of which would furnish 2 : 4 : 6 : 3' : 4'-pentamethoxy- $\alpha\alpha$ -diphenylpropane on reduction. The various stages in the synthesis of the chroman are as shown :

⁹⁰ S. Ruhemann, *Ber.*, 1921, **54**, [B], 912; *A.*, i, 430.

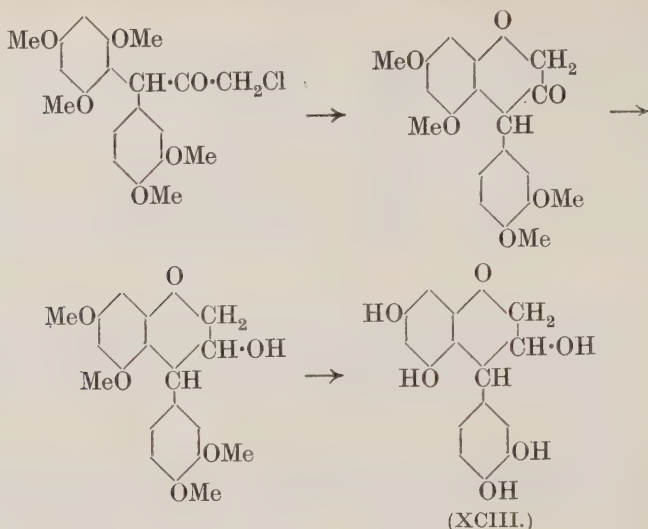
⁹¹ L. Claisen, *ibid.*, 200; *A.*, i, 263.

⁹² Compare *Ann. Reports*, 1920, **17**, 110.

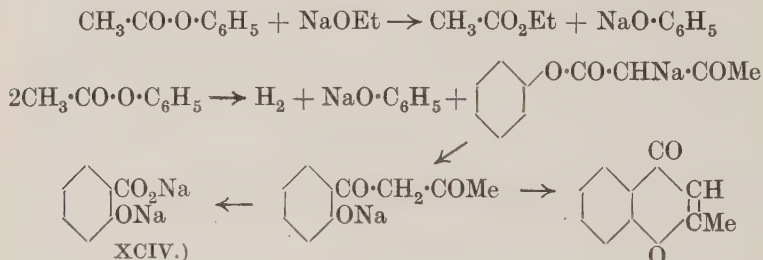
⁹³ K. Freudenberg, O. Böhme, and A. Beckendorf, *Ber.*, 1921, **54**, [B], 1204; *A.*, i, 576; K. Freudenberg, *Z. angew. Chem.*, 1921, **34**, 247; *A.*, i, 577.

⁹⁴ Compare also K. Feist and R. Schön, *Arch. Pharm.*, 1920, **258**, 317; *A.*, i, 47.

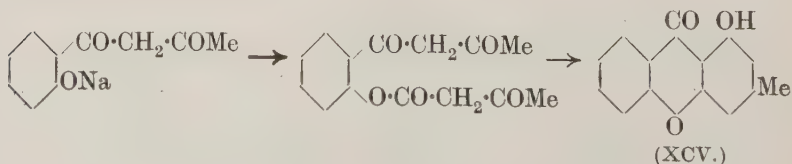
⁹⁵ M. Nierenstein, *T.*, 1921, **119**, 164.



A chromone has also been identified among the products of the action of sodium on phenyl acetate.⁹⁶ The mode of formation of 2-methylbenzo- γ -pyrone (XCIV), the compound in question, is represented by the following equations :

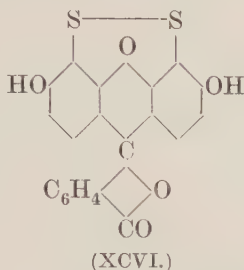


It may be noted that the production of ethyl acetate, dehydracetic acid, and salicylic acid in the course of the reaction has actually been demonstrated. 1-Hydroxy-3-methylxanthone (XCV) has also been isolated, its formation being due, it is supposed, to reactions represented as follows :



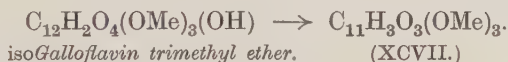
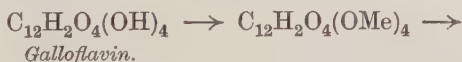
⁹⁶ W. H. Perkin, jun., *T.*, 1921, **119**, 1284.

Thiofluorescein, formed by the action of sodium sulphide on fluorescein at 110—150°, especially in presence of sodium hydroxide, has been shown to have been incorrectly designated,⁹⁷ and to have the formula (XCVI):⁹⁸



Condensation products of phenol and resorcinol with coumarin have been described, which give coloured salts and are probably analogues of phenolphthalein and fluorescein respectively.⁹⁹

Galloflavin, one of the products of oxidation of gallic acid in alkaline solution,¹ is considered to be derived from benzo- α -pyrone.² It is a non-acid substance, which suffers transformation by cold potassium hydroxide solution into *isogalloflavin*.³ Similarly, galloflavin tetramethyl ether, obtained by the aid of diazomethane,⁴ is converted into *isogalloflavin* trimethyl ether. This compound, from which the tetramethyl ether may be obtained, is a lactone and also contains a carboxyl group, which is destroyed by heating the substance at its melting point, with evolution of carbon dioxide and formation of the compound (XCVII):



The compound (XCVII), when treated with warm potassium hydroxide with the object of opening its lactone ring, furnishes potassium formate and a salt (XCVIII), which, on acidification with hot acid, yields a new lactone (XCIX) from which potassium

⁹⁷ R. E. Meyer and J. Szanecki, *Ber.*, 1900, **33**, 2577; *A.*, 1900, i, 660.

⁹⁸ T. Maki, *J. Coll. Eng. Tokyo Imp. Univ.*, 1920, **11**, 1; *A.*, i, 183.

⁹⁹ S. Krishna, *T.*, 1921, **119**, 1420.

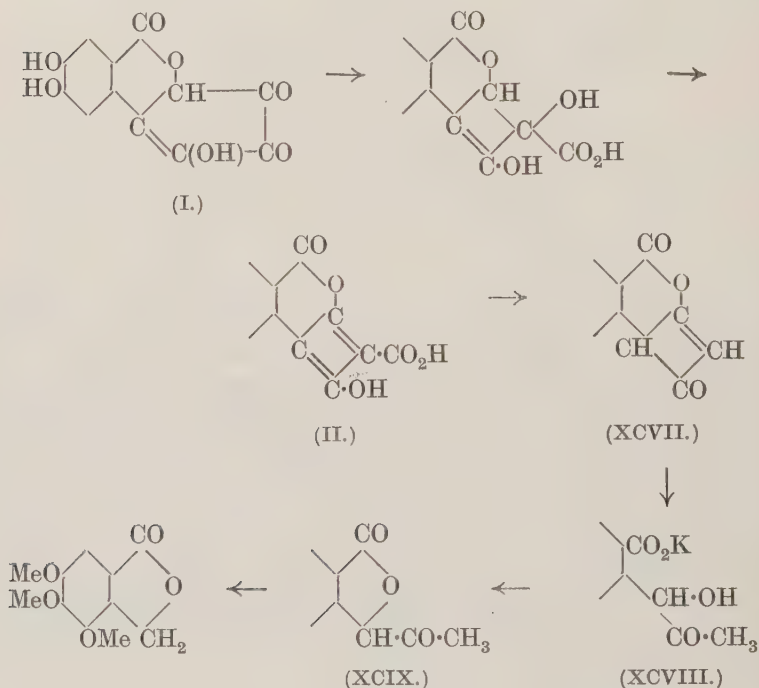
¹ R. Bohn and C. Graebe, *Ber.*, 1887, **20**, 2327; *A.*, 1887, 1107.

² J. Herzig, *Annalen*, 1920, **421**, 247; *A.*, 1920, i, 863.

³ J. Herzig and R. Wachslar, *Monatsh.*, 1914, **35**, 77; *A.*, 1914, i, 290.

⁴ J. Herzig and R. Tschorne, *ibid.*, 1904, **25**, 603; *A.*, 1904, i, 814.

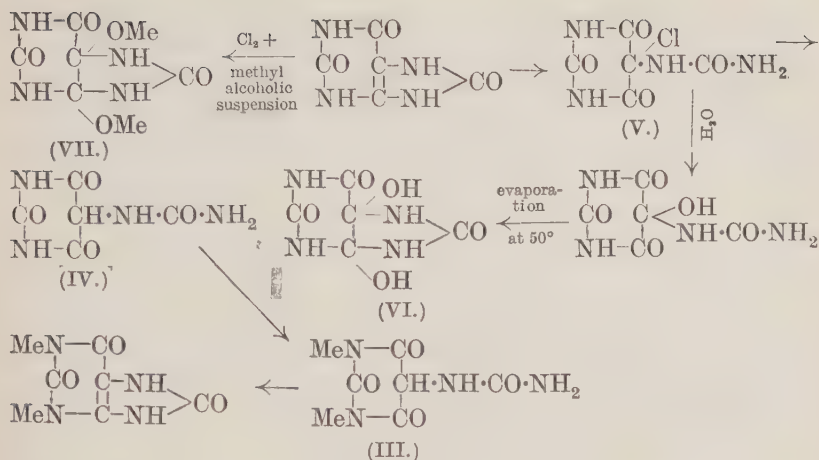
acetate and 3:4:5-trimethoxyphthalide are obtained by treatment with warm potassium hydroxide solution. From these various relationships, the formulæ (I) and (II) are deduced for galloflavin and isogalloflavin respectively :



Uric Acid and its Derivatives.

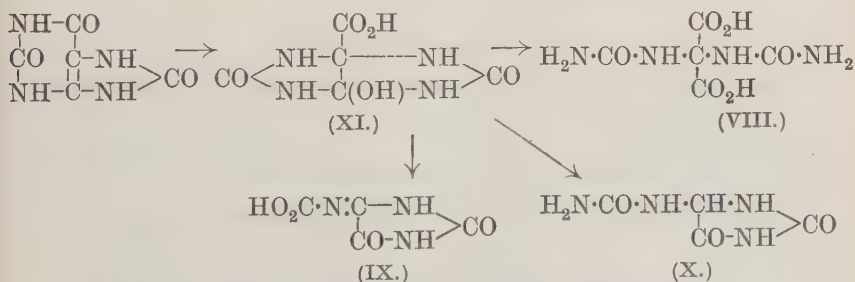
Reference has already been made to the formation of 1:3-dimethyluric acid, with other products, by direct alkylation of uric acid. This acid is conveniently accessible in the pure condition by dehydration of 1:3-dimethyl- ψ -uric acid (III), which is produced when ψ -uric acid (IV) is treated in alkaline solution with methyl sulphate.⁵ ψ -Uric acid itself is easily obtained by chlorination of uric acid in glacial acetic acid suspension at 5–10°, and reduction in situ of the resulting 5-chloro- ψ -uric acid (V) by stannous chloride :

⁵ H. Biltz and others, *Annalen*, 1921, **423**, 119; *A.*, i, 606.



Lack of space prevents more than reference to other items of a mass of experimental material dealing with the reactions (including alkylation) of the glycols (VI), and their ethers (VII), derived from uric acid and its alkyl derivatives by the reactions indicated.⁶

A series of papers⁷ is devoted to the discussion of the products obtained from uric acid by oxidation in alkaline solution with potassium permanganate. Potassium uroxanate (VIII) will be produced if the alkaline solution be concentrated and cooled. If, however, the solution be carefully acidified with acetic acid after the addition of alcohol, potassium oxonate (or allantoxanate) (IX) will be precipitated. Allantoin (X) will, however, be obtained if the acidified solution be left to itself, or concentrated and cooled. It is concluded that the sole intermediate product is hydroxydi-carbamidoethanecarboxylic acid (XI), the formation of which is the subject of an interesting discussion, which cannot be dealt with here :



⁶ H. Biltz and others, *Annalen*, 1916, **413**, 1; *A.*, 1917, i, 589.

⁷ H. Biltz and R. Robl, *Ber.*, 1920, **53**, [B], 1950, 1964, 1967; 1921, 54, [B], 2451; *A.*, 1920, i, 883, 884, 885; 1921, i, 891.

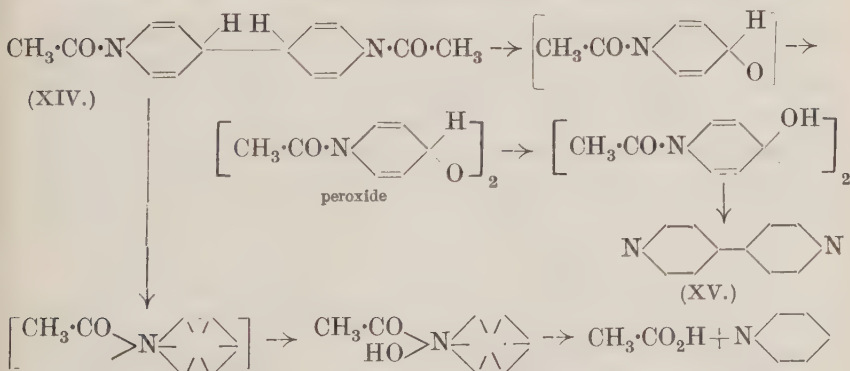
direct formation of this compound by the use of sodium hydrogen sulphite appears not to have been attempted.

At a bright red heat, pyridine is decomposed, yielding mainly 2 : 2'-, with smaller quantities of 2 : 3'- and 2 : 4'-dipyridyls.¹³

N-Alkylpiperidines and piperidine nitrate will be produced in the course of a few days by the interaction of piperidine with alkyl nitrates at the ordinary temperature.¹⁴

The synthesis of ethyl 2 : 6-dimethylcinchoneronate from ethyl acetylpyruvate and ethyl β -aminocrotonate¹⁵ has been shown¹⁶ to be capable of considerable, although limited, extension by the use of analogues of each of the reactants.

Several investigations deal with the partial reduction of the pyridine nucleus. Thus, by the reduction of pyridine with zinc dust and acetic anhydride,¹⁷ diacetotetrahydro- $\gamma\gamma$ -dipyridyl (XIV) is produced, the constitution of which is shown by its synthesis from $\gamma\gamma$ -dipyridyl (XV) by reduction with zinc dust and acetic anhydride, and by its conversion into this compound either by the action of moist air, or by oxidation with lead or manganese peroxide. This, it may be noted, is the most convenient method for preparing $\gamma\gamma$ -dipyridyl. Pyridine is the chief product of the oxidation of diacetotetrahydro- $\gamma\gamma$ -dipyridyl with a solution of iodine in potassium iodide. These results are explained by assuming the dissociation of the dipyridyl derivative in two ways :



In conformity with this view, the solution of diacetotetrahydro-dipyridyl in glacial acetic acid becomes deep blue on warming,

¹³ H. Meyer and (Miss) A. Hofmann-Meyer, *J. pr. Chem.*, 1921, [ii], 102, 287; *A.*, i, 739.

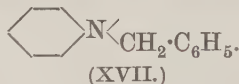
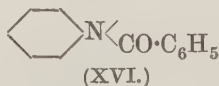
¹⁴ D. T. Gibson and A. K. Macbeth, *T.*, 1921, 119, 438.

¹⁵ *Ann. Reports*, 1918, 15, 101.

¹⁶ O. Mumm and O. Böhmer, *Ber.*, 1921, 54, [B], 726; *A.*, i, 439.

¹⁷ O. Dimroth and R. Heene, *ibid.*, 2934.

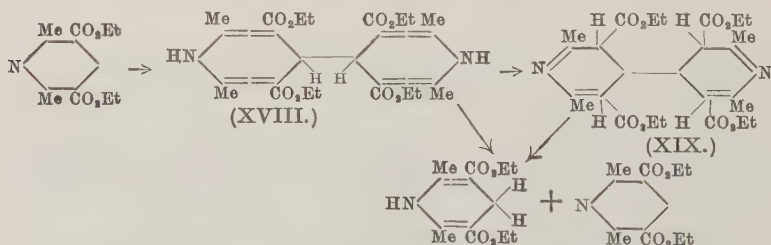
but is decolorised by air, thus showing a similar behaviour to solutions of triphenylmethyl. Again, by the action of zinc dust and benzoyl chloride¹⁸ on pyridine, benzoylpyridinium (XVI) is obtained in brown leaflets, which show the corresponding molecular weight in boiling ethylene dibromide or chlorobenzene solution, absorb oxygen from the air with consequent decolorisation, and react with halogens forming benzoic acid and $\gamma\gamma$ -dipyridyl. 1-Benzylpyridinium¹⁹ (XVII) has also been isolated in red crystals, furnishing deep blue methyl or ethyl alcoholic solutions; it is converted by halogens into 1-benzylpyridinium salts.



The partial reduction of certain pyridine derivatives has been accomplished by the aid of aluminium amalgam.²⁰ Thus ethyl collidine- and phenyl-lutidine-dicarboxylates yield the known synthetic 1:4-dihydro-derivatives,



but from ethyl lutidinedicarboxylate itself, a chrome-yellow "primary" ester (XVIII) is obtained, which is reconverted into the original compound on exposure to air at the ordinary temperature, yields it with its dihydro-derivative in equimolecular proportions when heated to its melting point, and furnishes a greenish-yellow "secondary" ester (XIX) on prolonged heating below its melting point in absence of air. The secondary compound is stable in air, but suffers a similar decomposition when fused:

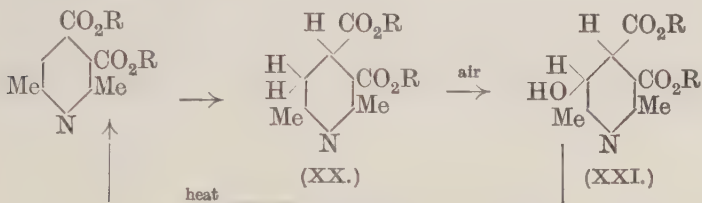


¹⁸ E. Weitz, A. Roth, and (Miss) A. Nelken, *Annalen*, 1921, **425**, 161; *A.*, **i**, 804.

¹⁹ E. Weitz, (Miss) A. Nelken (with R. Ludwig), *ibid.*, 187; *A.*, **i**, 804. Compare *Ann. Reports*, 1920, **17**, 106.

²⁰ O. Mumm and W. Beth, *Ber.*, 1921, **54**, [B], 1591; *A.*, **i**, 686.

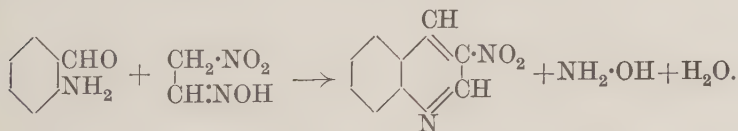
The reader will probably find it difficult to reconcile the formula (XX) suggested for the reduction product of ethyl 2:6-dimethyl-cinchomerone with the statement that it furnishes ammonia when treated with cold sodium ethoxide. By absorption of oxygen from the air, the compound in question is converted into a product, represented as (XXI), which loses water when heated, reproducing the original ester.



The Quinoline Group.

The yield of quinaldine is improved when the Doebner-Miller synthesis is carried out in presence of zinc chloride. At the same time, the presence of this reagent so enhances the tendency to the formation of Schiff's bases that the latter are produced in quantity sufficient to absorb the hydrogen which usually causes the production of tetrahydroquinaldine. Hence, in place of this compound, ethyl- and *n*-butyl-anilines are formed. The reason for the simultaneous formation of some 6-ethylquinaldine is for the time left undecided.²¹

The formation of 3-nitroquinolines by the condensation of *o*-aminobenzaldehyde or related compounds with methazonic acid²² seems to be simply a particular case of Friedländer's well-known synthesis :

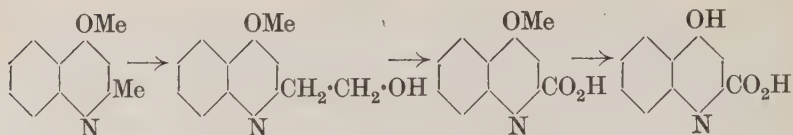


A new synthesis of 4-hydroxyquinoline-2-carboxylic (kynurenic) acid consists in the condensation of 4-methoxy-2-methylquinoline with formaldehyde, followed by oxidation of the 4-methoxy-2-quinolyethyl alcohol thus formed to 4-methoxyquinaldine acid, and subsequent demethylation of this product :²³

²¹ W. H. Mills, J. E. G. Harris, and H. Lambourne, *T.*, 1921, **119**, 1295.

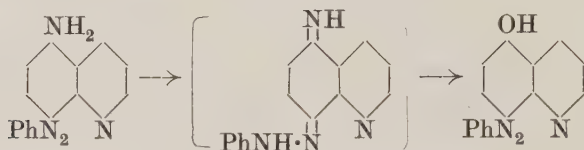
²² W. Meister, *Ber.*, 1907, **40**, 3435; B.A.S.F., D.R.-P. 335197; *A.*, 1907, i, 885; 1921, i, 517.

²³ E. Besthorn *ibid.*, 1921, **54**, [B], 1330; *A.*, i, 600.

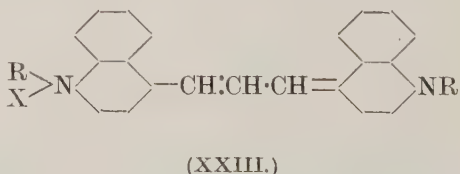
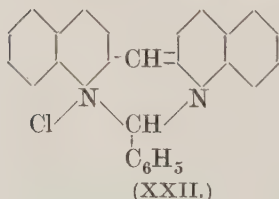


The reactivity of methyl groups in the methylquinolines is considerably greater in the 2- than in the 4-position.²⁴

The conversion of benzeneazo-5-aminoquinoline into the 5-hydroxy-derivative by boiling with dilute mineral acid for a short time²⁵ would seem to indicate that it easily assumes the quinoneimide form :



An examination²⁶ of the cyanines and the *isocyanines* has supported the conclusions summarised last year,²⁷ and indirect confirmation of these has been supplied by syntheses of the parent ψ -*isocyanine*, so called because its mode of formation from quinaldine corresponds with that of the *isocyanines* from lepidine. The ψ -compound results from the action of alcoholic potassium hydroxide on a mixture of 2-iodoquinolyl methiodide and quinaldine methiodide,²⁸ and also by the action of methyl iodide on *N*-methyl-2-quinolylenequinaldine, the synthesis of which has been discussed on p. 117. It is hoped that an application of the latter method will permit a synthesis of *isocyanine*. The formula for quinoline-red (XXII) seems an adequate expression of its synthesis by the action of benzal chloride on di-2-quinolylmethane.²⁹



²⁴ O. Fischer, G. Scheibe, P. Merkel, and R. Müller, *J. pr. Chem.*, 1919, [ii], **100**, 91; *A.*, i, 55.

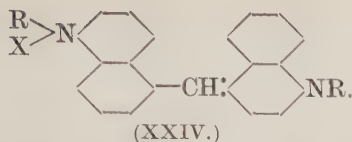
²⁵ W. A. Jacobs and M. Heidelberger, *J. Amer. Chem. Soc.*, 1920, **42**, 2278; *A.*, i, 44.

²⁶ W. König and O. Treichel, *J. pr. Chem.*, 1921, [ii], **102**, 63; *A.*, i, 738.

²⁷ *Ann. Reports*, 1920, **17**, 121.

²⁸ O. Fischer and G. Scheibe, *J. pr. Chem.*, 1919, [ii], **100**, 86; *A.*, i, 56.

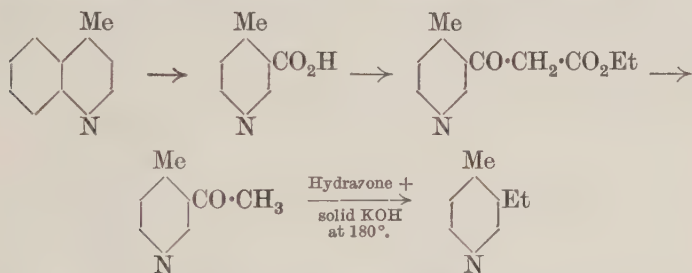
²⁹ G. Scheibe, *Ber.*, 1921, **54**, [B], 786; *A.*, i, 451.



Kryptocyanines are produced by the action of alkali on hot dilute alcoholic solutions of lepidine alkyl iodides in presence of formaldehyde or chloroform.³⁰ Since this reaction corresponds closely with that by which pinacyanol³¹ is produced from quinaldine ethiodide, it will probably be found that the new dyes have the formula (XXIII), rather than (XXIV) tentatively suggested by their discoverers.

Alkaloids.

Further progress has been made towards the synthesis of quinine and its derivatives along the lines indicated in last year's Report.³² Homonicotinic acid, obtained by the oxidation of lepidine, has been converted into β -collidine by the reactions indicated :³³



The method previously successfully applied to the synthesis of β -4-piperidylpropionic acid has been extended to the conversion of β -collidine into homocincholeupone,³⁴ and protection has been obtained for the process whereby the latter compound is utilised for the preparation of dihydro-cinchoninone and -quininone.³⁵ A general method³⁶ for the reduction of 4-quinolyl ketones by zinc or aluminium powder and sodium ethoxide has the advantage that it leaves unchanged the unsaturated side-chain in, for example, quininone. Its application to dihydrocinchoninone results in the

³⁰ E. A. Adams and H. L. Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2661; *A.*, i, 129.

³¹ Compare *Ann. Reports*, 1920, **17**, 122.

³² P. 117.

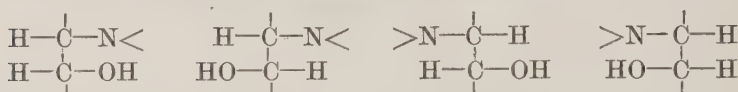
³³ P. Rabe and E. Jantzen, *Ber.*, 1921, **54**, [B], 925; *A.*, i, 438.

³⁴ E. Koenigs and W. Ottmann, *ibid.*, 1343; *A.*, i, 595.

³⁵ Ver. Chinin-Fabr. Zimmer & Co., D.R.-P. 330945; *A.*, i, 360; compare *Ann. Reports*, 1920, **17**, 118.

³⁶ *Idem*, D.R.-P. 330813; *A.*, i, 355.

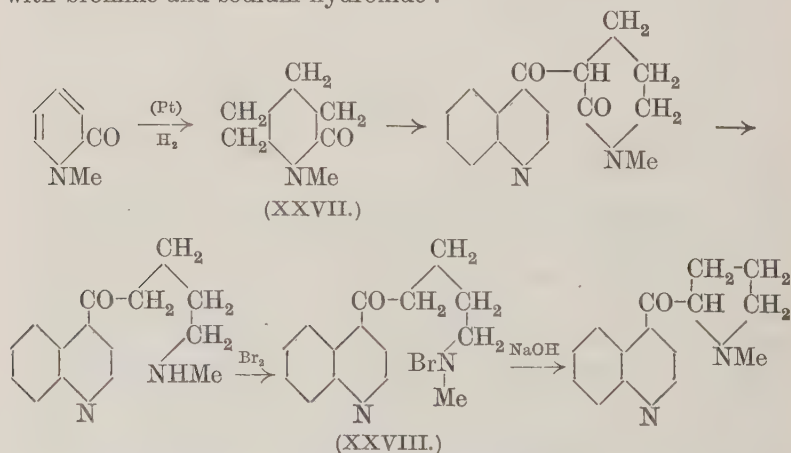
formation of the four possible isomerides, of which the relationship may be represented by the following symbols :



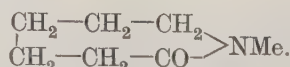
Of these, two correspond with the minor cinchona alkaloids; the remaining two, which were previously unknown, may be reconverted by known methods through dihydrocinchotoxine into the original dihydrocinchoninone.

Space does not permit of more than passing reference to the interesting results of the action of bromine on dihydroquinine and dihydrocupreine,³⁷ and of diazotising 5-aminocinchona alkaloids.³⁸

Previous syntheses of compounds closely related to quinine have been supplemented by those of the compounds (XXV) and (XXVI).³⁹ Thus, 1-methyl-2-pyridone was converted by catalytic reduction into the lactam of δ -methylaminovaleric acid (XXVII). It was not previously known that such lactams are amenable to the Claisen condensation. In the present case, the compound (XXVIII) was synthesised by this means, and treated successively with bromine and sodium hydroxide :



In a similar manner, a homologue of (XXVIII) is obtained from ϵ -methylaminohexoxic lactam,

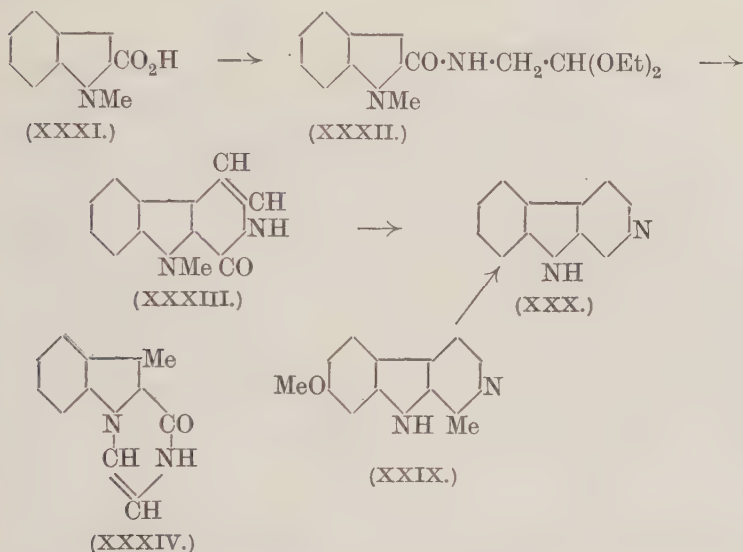


³⁷ R. Weller, *Ber.*, 1921, **54**, [B], 230; *A.*, i, 265.

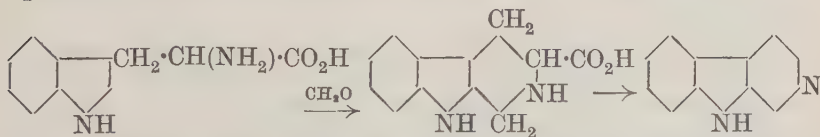
³⁸ G. Giemsa and J. Halberkann, *ibid.*, 1167; *A.*, i, 581.

³⁹ L. Ruzicka and C. T. Seidel, *Helv. Chim. Acta*, 1921, **4**, 472; *A.*, i, 585.

The suggestion that harmine is a methylmethoxy-4-carboline⁴⁰ (XXIX) is now confirmed⁴¹ by its degradation to norharman (4-carboline) (XXX) by two separate methods, and the synthesis of the latter compound. 1-Methylindole-2-carboxylic acid (XXXI) is converted through its chloride into 1-methylindole-2-carboxy-acetylamide (XXXII), which, when treated with alcoholic hydrochloric acid, furnishes 5-keto-4 : 5-dihydroindolediazine (XXXIII), from which norharman is obtained by distillation with zinc dust :



A synthesis of norharmine on similar lines is foreshadowed. The necessity for using *N*-methylindole derivatives arises from the fact that the unmethylated compound gives rise to 5-keto-7-methyl-4 : 5-dihydroindolediazine(1 : 4) (XXXIV). Norharman also results from the condensation of tryptophan with formaldehyde in presence of sulphuric acid, followed by oxidation of the product :



Since harman (with which the alkaloids aribine,⁴² loturine, and,

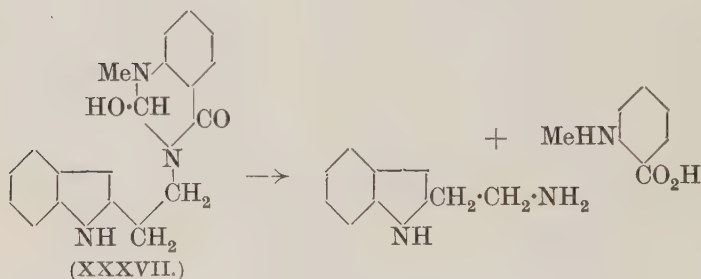
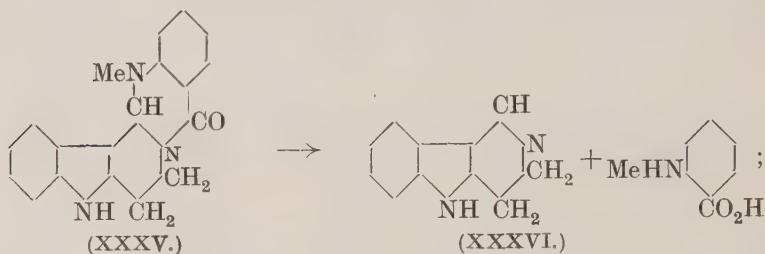
⁴⁰ *Compte Ann. Reports*, 1919, **16**, 122.

⁴¹ W. O. Kermack, W. H. Perkin, jun., and R. Robinson, *T.*, 1921, **119**, 1602.

⁴² E. Späth, *Monatsh.*, 1919, **40**, 351; *A.*, 1920, **i**, 327.

possibly, colloturine⁴³ have been identified) is obtained in a similar manner by the use of acetaldehyde, the position of the methyl group in this and in harmine is determined.

Evodiamine (XXXV) is broken down by boiling alcoholic potassium hydroxide into *N*-methylantranilic acid and a base. This is considered to be 3:4-dihydro-5-carboline (XXXVI),



because "*isoevodiamine*" (XXXVII) (obtained from evodiamine by boiling with two per cent. alcoholic hydrochloric acid) is similarly decomposed into *N*-methylantranilic acid and a base, thought to be 2- β -aminoethylindole, since it yields 2-indolecarboxylic acid on fusion with potassium hydroxide.⁴⁴ It has been pointed out,⁴⁵ however, that the last piece of evidence is inconclusive, since the same acid is one of the products of the alkaline fusion of scatole(3-methylindole), and, further, that it is improbable that derivatives of 5- as well as of 4-carboline should occur naturally.

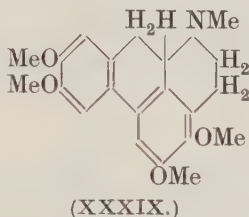
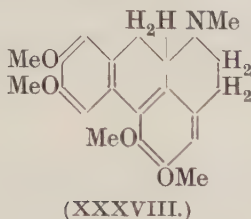
Laurotetanine is a phenolic secondary base, which readily oxidises. It is converted by "nascent" diazomethane into its methyl ether, but by preformed diazomethane into *N*-methyl-laurotetanine methyl ether, which is designated *isoglaucine* owing

⁴³ E. Späth, *Monatsh.*, 1920, **41**, 297; *A.*, i, 50.

⁴⁴ Y. Asahina and S. Mayeda, *J. Pharm. Soc. Japan*, 1916, No. 416; *A.*, i, 48.

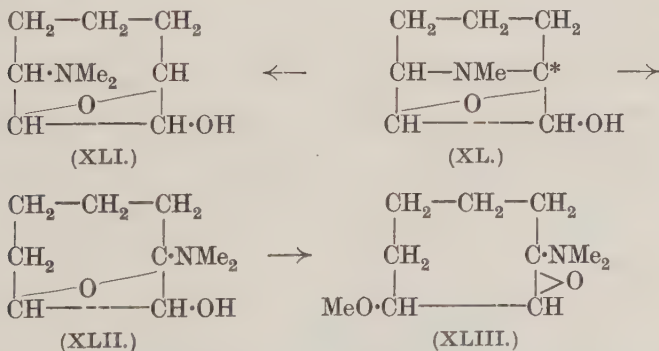
⁴⁵ W. O. Kermack, W. H. Perkin, jun., and R. Robinson, *loc. cit.*

to its isomerism with, and similarity to, glaucine (XXXVIII).⁴⁶ For this reason, and in view of the oxidation of laurotetanine to 1:2-dimethoxybenzene-3:4:5-tricarboxylic acid, the formula (XXXIX) is assigned to *isoglaucine*:⁴⁷



A more detailed account of the synthesis of ecgonine outlined in last year's Report has since been published.⁴⁸

A reinvestigation⁴⁹ of the degradation of scopoline by exhaustive methylation has shown that it proceeds normally under very low pressure if silver be excluded from solution. The product is not however, uniform, since a mixture of four dihydrodemethylscopolines is obtained by reducing it. One of these, a crystalline compound, is unchanged by treatment with sodium methoxide, whilst from the oily mixture of the remaining three a product (XLIII) is obtained corresponding with *O*-methyl-*iso*- ψ -demethylscopoline. This is attributed to the presence in the original mixture of the compound (XLII), corresponding in structure with ψ -demethylscopoline:



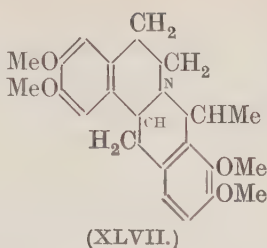
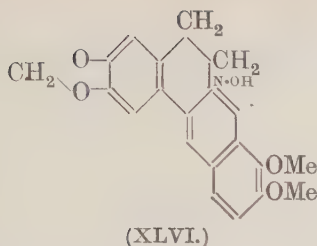
Against the formula (XL) for scopoline it has been urged that

⁴⁶ Compare J. Gadamer, *Arch. Pharm.*, 1911, **249**, 680; *A.*, 1912, i, 48.

⁴⁷ K. Gorter, *Bull. Jard. bot. Buitenzorg*, 1921, [iii], **3**, 180; *A.*, i, 587.

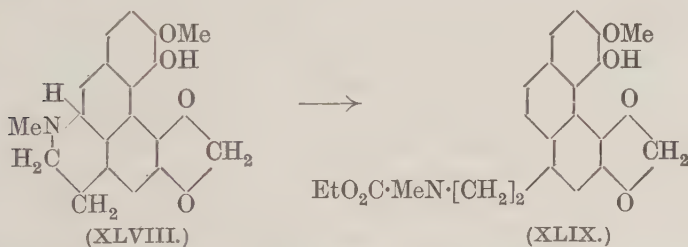
⁴⁸ R. Willstätter and M. Bommer, *Annalen*, 1921, **422**, 15; *A.*, i, 122.

⁴⁹ K. Hess, *Z. angew. Chem.*, 1921, **34**, 393; *A.*, i, 683.



By the action of sulphaacetic acid on papaverine, the sulphaacetate of a new base, coralyne, is obtained. This compound is so named owing to its close relationship to the synthetic coralydine, into the α -form of which it has been converted by reduction.⁵⁶

Passing reference may be made to a discussion of the mutual relationships of the *isoquinoline* alkaloids.⁵⁷ Ethyl chloroformate promises to be a useful reagent for the investigation of these compounds, since it has been found to break down the tetrahydro-*isoquinoline* ring, but to have little effect on the dihydroindole, pyrrolidine, piperidine, and tetrahydroquinoline rings.⁵⁸ For example, bulbocapnine (XLVIII) is converted into ethyl bulbocapninecarboxylate (XLIX) :



In the morphine group, attention is being concentrated on a study of the various reduction products obtainable from thebaine and codeine, and their derivatives.⁵⁹

J. KENNER.

⁵⁶ W. Schneider and K. Schroeter, *Ber.*, 1920, **53**, [B], 1459; *A.*, i, 760; W. Schneider and A. Köhler, *ibid.*, 1921, **54**, [B], 2031; *A.*, i, 803.

⁵⁷ J. W. D. Hackh, *Chem. News*, 1921, **123**, 178; *A.*, i, 800.

⁵⁸ J. Gadamer and F. Knoch, *Arch. Pharm.*, 1921, **259**, 135; *A.*, i, 579.

⁵⁹ C. Mannich and (Miss) H. Löwenheim, *ibid.*, 1920, **258**, 295; M. Freund and E. Speyer, *Ber.*, 1920, **53**, [B], 225; A. Skita, *ibid.*, 1921, **54**, [B], 1560; E. Speyer and S. Siebert, *ibid.*, 1519; E. Speyer and others, D.R.-P. 338147; *A.*, i, 124, 125, 684, 685, 803.

ANALYTICAL CHEMISTRY.

THE analytical work published during the past year has been greater in volume and more diverse in character than in any other year since the outbreak of the war. Hence, in order to confine a general survey within the space available, it has been necessary to make a selection from the more important contributions, and to omit many which would otherwise have received notice.

Physical Methods.

The influence of adsorption on the accuracy of analytical results has been demonstrated in a series of papers. For example, filter-paper adsorbs a considerable proportion of lead, and smaller amounts of copper and silver. The main cause of this is the mineral matter in the paper, and the presence of an acid solution (that is, hydrogen ions) prevents the adsorption.¹ The amount of acid adsorbed by filter-paper is equivalent to the alkalinity of the ash.² The amounts of alkali taken up are directly proportional to the alkalinity of the solution, but in this case there is no true adsorption.³ The removal of heavy metals by cellulose is due to a chemical reaction, and is not a physical process.⁴ The use of impure asbestos leads to error owing to the adsorption of positive ions. Advantage may be taken of this fact for the estimation of lead in water.⁵ The absorption of salts of metals or of alkaloids by glass-wool appears to be due to the alkalinity of the glass, and the loss may be considerable if this material is used for the filtration of hot solutions.⁶ Reference may also be made, in this connexion, to the influence of the glass of certain bottles of recent manufacture on standard acid and other solutions.⁷

Several new methods of analysis have been based on the determination of the temperature of miscibility of two or more liquids. For example, the alcoholic strength of aqueous alcohol may be rapidly ascertained by mixing the liquid with acetone or light

¹ I. M. Kolthoff, *Pharm. Weekblad*, 1920, **57**, 1510; *A.*, ii, 19.

² *Idem, ibid.*, 1571; *A.*, ii, 123.

³ *Idem, ibid.*, 1921, **58**, 46; *A.*, ii, 213.

⁵ *Idem, ibid.*, 401; *A.*, ii, 344.

⁷ C. A. Mitchell, *Analyst*, 1921, **46**, 129.

⁴ *Idem, ibid.*, 233; *A.*, ii, 277.

⁶ *Idem, ibid.*, 463; *A.*, ii, 409.

petroleum,⁸ and in the case of ternary mixtures, such as alcohol, ether, and water, the composition may be found from the quantity of water required to produce turbidity, or of ether to obtain a clear liquid.⁹ Similarly, the critical temperature of solution in aniline of light petroleum, before and after nitration, affords a measure of the hydrocarbons present.¹⁰ The lowering of the temperature at which a mixture of hydrocarbons and aniline separates into two layers, after sulphonation, corresponds directly with the proportion of aromatic hydrocarbons in the mixture.¹¹

The use of nephelometric methods has been extended in several directions, and a new type of nephelometer has been constructed, in which the height of a standard Tyndall cone is measured in the liquid under examination and in a standard solution. In all such measurements, it is essential that the particles of the turbid liquid should be of uniform size.¹² For certain biochemical estimations, the turbidimeter of Folin and Denis¹³ is preferable to the nephelometer.¹⁴

An addition to the numerous applications of refractometry in analytical work has been published, the principle having been adapted to the calculation of the proportions of salts in an aqueous solution.¹⁵

For the spectroscopic examination of mixtures, the use of the X-ray spectrum has the advantage of relative simplicity as compared with the ordinary spectrum. A vacuum spectrograph has been devised, by means of which photographs of the lines of all the elements may be readily obtained.¹⁶

There have not been many contributions to the methods of determining viscosity, but reference may be made to the cup-and-ball viscosimeter, in which the time before a ball falls from an inverted cup in which a drop of the oil has been placed is measured. This gives results comparable with those obtained with standard apparatus.¹⁷

⁸ H. Rosset, *Ann. Chim. anal.*, 1921, [ii], 3, 235; *A.*, ii, 598.

⁹ L. Desvergues, *Mon. Sci.*, 1921, 11, 145; *A.*, ii, 601.

¹⁰ G. Chavanne and L. J. Simon, *Ann. Chim. anal.*, 1921, [ii], 3, 87; *A.*, ii, 354.

¹¹ H. T. Tizard and A. G. Marshall, *J. Soc. Chem. Ind.*, 1921, 40, 20T; *A.*, ii, 280.

¹² H. Kleinmann, *Kolloid Z.*, 1920, 27, 236; *A.*, ii, 56.

¹³ O. Folin and W. Denis, *J. Biol. Chem.*, 1914, 18, 263; *A.*, 1914, ii, 687.

¹⁴ W. Denis, *ibid.*, 1921, 47, 27; *A.*, ii, 555.

¹⁵ C. A. Clemens, *J. Ind. Eng. Chem.*, 1921, 13, 813; *A.*, ii, 650.

¹⁶ M. Siegbahn, A. E. Lindh, and N. StenSSon, *Z. Physik*, 1921, 4, 61; *A.*, ii, 344.

¹⁷ T. C. Thomsen, *Report of Lubrication Inquiry Committee, Dept. Scientific and Ind. Research*, 1920, 15—16, 103.

A new instrument for determining the surface tension of liquids from the rise in capillary tubes has been devised, and is intended especially for cases where only a small amount of the liquid is available.¹⁸

Gas Analysis.

Several new forms of apparatus for use in gas analysis have been designed. One of these is an absorption vessel the stopper of which is hollow and has a perforated extension reaching nearly to the bottom of the flask, and the gas is made to pass through this stopper on its way through the absorbent.¹⁹ Another apparatus is a gas-volume compensator, by means of which the volume of a constituent absorbed from a gas may be obtained with an accuracy of within 0.5 per cent. from the reading shown on a manometer.²⁰

A new method for the estimation of microscopically small quantities of gas has been based on the consecutive determination of the condensation temperature of each gas when cooled in the side tube of a Pirani gauge. In practice, the results are compared with those obtained with a series of gauges each containing a pure gas, and the respective amounts are found by reference to graphs.²¹

The methods principally used for the estimation of small quantities of carbon monoxide in air are those based on its oxidation by means of iodic anhydride,²² and on its conversion into carboxyhæmoglobin.²³ Elimination of the influence of other gases reacting with iodic anhydride is not always easy; for this reason, the second method is often preferable, but air containing more than 0.1 per cent. of carbon monoxide must be diluted before being passed through the hæmoglobin solution.²⁴

A reagent termed "Hoolamite" (U.S. Pats. 1321061—2) consists of a mixture of iodic anhydride, fuming sulphuric acid, and pumice stone. The carbon dioxide formed in the oxidation of the carbon monoxide reacts with the excess of sulphur trioxide to form a green compound, and the intensity of the coloration, when compared with special colour standards, affords a measure of the carbon monoxide. The method is applicable to gases containing up to 0.2 per cent. of carbon monoxide.²⁵

¹⁸ S. Sugden, *T.*, 1921, **119**, 1483.

¹⁹ Walz, *Chem. Ztg.*, 1921, **45**, 658; *A.*, ii, 515.

²⁰ R. S. Tour, *Chem. Met. Eng.*, 1920, **23**, 1104; *A.*, ii, 125.

²¹ Research Staff, Gen. Electric Co., Ltd. (W. R. Campbell), *Proc. Physical Soc.*, 1921, **33**, 287; *A.*, ii, 591.

²² A. Gautier, *Compt. rend.*, 1898, **126**, 793; *A.*, 1898, ii, 537.

²³ J. Ogier and E. Kohn-Abrest, *Ann. Chim. anal.*, 1908, **13**, 169; *A.*, 1908, ii, 631.

²⁴ D. Florentin and H. Vandenberghe, *Compt. rend.*, 1921, **172**, 391; *A.*, ii, 276.

²⁵ C. R. Hoover, *J. Ind. Eng. Chem.*, 1921, **13**, 770; *A.*, ii, 654.

Two modifications of the Pettenkofer method of estimating carbon dioxide in air have been devised, the gas in each case being absorbed by standard sodium hydroxide solution, the excess of which is subsequently titrated.²⁶

A gravimetric method of estimating nitrous fumes in air, etc., has been based on the formation of an orange precipitate when a solution of a nitrite is heated at 50° first with a solution of *p*-nitroaniline and then with an alkaline solution of α -naphthol.²⁷

The fact that iodine converts metals such as silver, copper, or aluminium into iodides at the ordinary temperature has been utilised for the detection of chlorine in air. When a sheet of silver forming part of an electric circuit is covered with damp potassium iodide any chlorine present in the air will liberate iodine, which will then combine with the metal, and break the electric circuit; this may be notified audibly by the addition of a suitable device.²⁸

It has been shown that adsorption of small quantities of benzene hydrocarbons in coal gas by means of charcoal, and their subsequent distillation with steam, give more accurate results than are obtainable by the dinitrobenzene or paraffin methods.²⁹

Agricultural Analysis.

Various methods for the estimation of colloidal material in soil have been published. One of these, depending on a physical separation of "ultra clay" by centrifugal action, gave results in agreement with those calculated from the absorption of dry ammonia by the soil.³⁰

Considerable attention has also been directed to the estimation of hydrogen-ion concentration as an indication of the lime requirement of soils. A convenient colorimetric method has been devised, and in using this for estimating the lime requirement increasing quantities of barium hydroxide are added to the soil, prior to the extraction, a curve plotted of the successive hydrogen-ion concentrations, and the amounts of barium hydroxide calculated into calcium oxide.³¹

The method of estimating soil acidity by the liberation of iodine from a solution of potassium iodide and iodate³² has been shown to be influenced by too many factors to be really trustworthy.³³

²⁶ J. Freund, *Z. Hyg.*, 1920, **91**, 218; *A.*, ii, 348.

²⁷ J. Moir, *J. S. African Assoc. Anal. Chem.*, 1921, **4**, 3; *A.*, ii, 345.

²⁸ C. Matignon, *Compt. rend.*, 1921, **172**, 532; *A.*, ii, 272.

²⁹ E. Berl, K. Andress, and W. Müller, *Z. angew. Chem.*, 1921, **34**, 125; *A.*, ii, 272.

³⁰ C. J. Moore, W. H. Fry, and H. E. Middleton, *J. Ind. Eng. Chem.*, 1921, **13**, 527; *A.*, ii, 608.

³¹ E. A. Fisher, *J. Agric. Sci.*, 1921, **11**, 45; *A.*, ii, 349.

³² A. Stutzer and W. Haupt, *J. Landw.*, 1915, **63**, 33; *A.*, 1915, ii, 655.

³³ O. Lemmermann and L. Fresenius, *ibid.*, 1921, **69**, 97; *A.*, ii, 516.] 

A new method of estimating potassium in soils, even in the presence of considerable amounts of sodium salts, depends on its precipitation as cobaltinitrite, and measurement of the volume of the precipitate.³⁴ The method of Folin and Macallum³⁵ does not give accurate results unless the soil is suspended in a saturated salt solution.³⁴

A rapid test for readily-soluble phosphates in soils is based on the extraction of the air-dried sample with standard nitric acid, precipitation of the phosphate with ammonium molybdate at 60°, and measurement of the amount of the precipitate.³⁶

Apparently the presence of other salts in the soil retards the precipitation of the magnesium ammonium phosphate in the estimation of citric-soluble phosphate, and the liquid should therefore be left over-night before filtration.³⁷

A micro-Kjeldahl method, which enables nitrogen to be estimated in a few mg. of material, has been described; methyl-red is used as the indicator in the titration.³⁸

For the estimation of ammoniacal nitrogen in fertilisers containing calcium cyanamide and ammonium salts, the solution is treated with sodium hydroxide and a current of air aspirated through it into standard acid for about seven hours at the ordinary temperature.³⁹

A direct method of estimating dicyanodiamide in mixed fertilisers depends on its precipitation with silver picrate, which does not give a precipitate with cyanamide or carbamide.⁴⁰ An analogous method has been based on the precipitation of a compound of 2 mols. of dicyanodiamide with 1 mol. of silver picrate, whilst carbamide and dicyanodiamidine are not precipitated. Dicyanodiamide also forms similar silver complexes with soluble nitrophenols, such as the silver salt of trinitroresorcinol, which gives even more accurate results than silver picrate.⁴¹

The principle may also be used as the basis of a volumetric process, the excess of silver remaining after the precipitation of the complex silver picrate dicyanoguanidine being titrated.⁴²

³⁴ O. Arrhenius, *Medd. K. Vetenskapakad., Nobel-Inst.*, 1920, **4**, 1; *A.*, ii, 412.

³⁵ O. Folin and A. B. Macallum, *J. Biol. Chem.*, 1912, **11**, 523; *A.*, 1912, ii, 683.

³⁶ O. M. Shedd, *Soil Sci.*, 1921, **11**, 111; *A.*, ii, 274.

³⁷ P. Müller, *Chem. Ztg.*, 1921, **45**, 178; *A.*, ii, 275.

³⁸ W. Geilmann, *J. Landw.*, 1920, **68**, 235; *A.*, ii, 128.

³⁹ J. Froidevaux and H. Vandenberghé, *Ann. Chim. anal.*, 1921, **3**, 146; *A.*, ii, 462.

⁴⁰ R. N. Harger, *J. Ind. Eng. Chem.*, 1920, **12**, 1107; *A.*, ii, 224.

⁴¹ E. B. Johnson, *J. Soc. Chem. Ind.*, 1921, **40**, 125; *A.*, ii, 468.

⁴² *Idem*, *J. Ind. Eng. Chem.*, 1921, **13**, 533; *A.*, ii, 605.

Carbamide in fertilisers may be accurately estimated by precipitation as carbamide oxalate, which is then purified, dried under reduced pressure, and weighed.⁴²

Organic Analysis.

Qualitative.—Some new sensitive colour reactions with alkaline phenylhydrazine hydrochloride solution containing metal or diazobenzenesulphonic acid have been devised for the identification of formaldehyde and acetaldehyde.⁴³ Resorcinol with sulphuric acid is also a very sensitive reagent for formaldehyde after separation in a current of steam.⁴⁴ In this way, the test may be used in the presence of tartaric and oxalic acids, which also give colorations with the reagent.⁴⁵

Further work has been done on the identification of organic acids by conversion into their phenacyl esters, which are then separated by fractional crystallisation.⁴⁶

Lactic acid gives a characteristic red coloration with alcoholic guaiacol solution, and may thus be distinguished from formic, acetic, malic, benzoic, salicylic, and certain other acids.⁴⁷

A method for the detection of free tartaric acid in wines has been based on its partial extraction with amyl alcohol, in which potassium hydrogen tartrate and calcium tartrate are insoluble.⁴⁸

The biochemical process of detecting dextrose⁴⁹ has been found a suitable means for the examination of plant material.⁵⁰ A reagent giving a brown coloration with woody fibre and with vanillin consists of a solution of vanadium pentoxide in phosphoric acid solution; it may be used as a microscopic test.⁵¹

Phenol may be identified by giving a characteristic, coloured zone when mixed with sodium nitrite solution and poured on to the surface of sulphuric acid.⁵²

A test capable of detecting 1 part of fluorescein in 200,000,000 parts consists in acidifying the solution with sulphuric or hydrochloric acid, shaking it with ether, and, after separation of the

⁴² E. B. Johnson, *J. Ind. Eng. Chem.*, 1921, **13**, 533; *A.*, ii, 605.

⁴³ E. Pittarelli, *Arch. Farm. Sperim. Sci. Aff.*, 1920, **30**, 148; *A.*, ii, 222.

⁴⁴ R. Cohn, *Chem. Ztg.*, 1921, **45**, 997; *A.*, ii, 663.

⁴⁵ E. Krausz and H. Tampke, *ibid.*, 521; *A.*, ii, 466.

⁴⁶ J. B. Rather and E. E. Reid, *J. Amer. Chem. Soc.*, 1921, **43**, 629; *A.*, ii, 356. Compare *A.*, 1920, i, 381.

⁴⁷ E. Hartwig and R. Saar, *Chem. Ztg.*, 1921, **45**, 322; *A.*, ii, 356.

⁴⁸ L. Mathieu, *Ann. Falsif.*, 1921, **14**, 281; *A.*, ii, 662.

⁴⁹ Compare *Ann. Reports*, 1920, **17**, 138.

⁵⁰ M. Bridel and R. Arnold, *Compt. rend.*, 1920, **172**, 1434; *A.*, ii, 465.

⁵¹ J. Grüss, *Ber. Deut. bot. Ges.*, 1921, **38**, 361; *A.*, ii, 284.

⁵² G. Rodillon, *J. Pharm. Chim.*, 1921, [vii], **23**, 136; *A.*, ii, 282.

ethereal layer, adding a few drops of ammonia, when a green coloration is produced when fluorescein is present.⁵³

The green coloration produced by concentrated sulphuric acid with certain lactic and cinnamic acid derivatives is due to the formation of indones, which combine with the sulphuric acid, whereas hydrindones do not give the reaction. It is possible in this way to distinguish between stable cinnamic acids and *allo*-compounds.⁵⁴

Methods of distinguishing between volatile alkylamines and ammonia, and between volatile tertiary and primary or secondary alkylamines have been based on their respective behaviour with formaldehyde, and with potassium mercuric iodide.⁵⁵

Glycine anhydride, creatinine, and some allied compounds give a coloration when heated with picric acid; this reaction, however, is also given by numerous other substances.⁵⁶

It has been shown the thalleioquinine reaction is most sensitive when the proportion of bromine is as 6 atoms per molecule of quinine; it is capable of detecting 1 part of the alkaloid in 250,000 parts.⁵⁷

Theobromine may be distinguished from caffeine by the differences in the colorations produced when the respective bismuthiodides are reduced by means of hydriodic acid.⁵⁸

Hitherto no definite colour reaction of aconite has been known, but it has recently been shown that aconitine, or at all events ψ -aconitine, the alkaloid in Indian aconite, gives a distinctive green coloration with potassium ferricyanide and formic acid.⁵⁹

A new method of distinguishing between ouabain and strophanthin is based on the difference in the behaviour of the two glucosides when warmed with hydrochloric acid and resorcinol. Strophanthin gives a rose coloration, whilst ouabain gives no coloration, this difference being due to the action of the respective sugars formed in the hydrolysis.⁶⁰

No distinctive test for vitamins has yet been discovered, but it has been found that some constituent of antiscorbutic extracts, possibly a polyphenol readily detached from a vitamin, gives a blue coloration with a sulphuric acid solution of sodium tungstate,

⁵³ M. Lombard, *Bull. Soc. chim.*, 1921, [iv], **29**, 462; *A.*, ii, 528.

⁵⁴ R. de Fazi, *Gazzetta*, 1921, **51**, i, 164; *A.*, ii, 357.

⁵⁵ H. E. Woodward and C. L. Alsberg, *J. Biol. Chem.*, 1921, **46**, 1; *A.*, ii, 358.

⁵⁶ T. Sasaki, *Biochem. Z.*, 1921, **114**, 63; *A.*, ii, 358.

⁵⁷ W. B. Hart, *J. Soc. Chem. Ind.*, 1921, **40**, 72T; *A.*, ii, 359.

⁵⁸ M. Malmy, *J. Pharm. Chim.*, 1921, [vii], **23**, 89; *A.*, ii, 360.

⁵⁹ S. Mallaneh, *Analyst*, 1921, **46**, 193; *A.*, ii, 470.

⁶⁰ A. Richaud, *J. Pharm. Chim.*, 1921, **24**, 161; *A.*, ii, 601.

phosphomolybdic acid, and phosphoric acid. Extracts which do not possess antiscorbutic properties do not give this coloration, which, however, is also produced by quinol.⁶¹

Quantitative.—Two new types of combustion furnace have been designed, one of which has many advantages over the ordinary furnace,⁶² whilst the other is a compact micro-furnace, which can also be used for the estimation of nitrogen.⁶³

A new method for the estimation of enols has been based on the fact that they form complex copper salts which are soluble in chloroform,⁶⁴ but it has been shown that the method is only applicable to a very limited number of cases.⁶⁵

Simple volatile alcohols may be estimated by esterification with lauryl chloride, extraction of the ester with ether, and its hydrolysis with potassium hydroxide, but the method is not satisfactory with secondary alcohols of the type of menthol.⁶⁶

A rapid method of estimating ethyl alcohol is to add aniline and to titrate the liquid with water until a permanent turbidity results, the volume of alcohol being then found by reference to a graph.⁶⁷

For the estimation of ethyl acetoacetate advantage has been taken of the fact that the ester reacts with sodium sulphite, with the liberation of sodium hydroxide, which is subsequently titrated.⁶⁸

It has been shown that the accuracy of the iodometric method of estimating acetone depends mainly on the proportion of potassium hydroxide added to the solution.⁶⁹

A new method of estimating glycerol in wines depends on its conversion into acetaldehyde by means of boric acid, and estimation of the distilled aldehyde by means of standard silver nitrate solution.⁷⁰

There have been but few additions to the methods of analysing oils and fats, but it has been shown that propyl alcohol is a useful medium for obtaining complete substitution in the determination of the bromine-substitution value.⁷¹ A simple and trustworthy formula for calculating the acetyl value from the saponification

⁶¹ N. Bezssonoff, *Compt. rend.*, 1921, 173, 466; *A.*, ii, 608.

⁶² T. J. Hedley, *T.*, 1921, 119, 1242.

⁶³ W. Dautwitz, *Chem. Ztg.*, 1920, 44, 963; *A.*, ii, 131.

⁶⁴ W. Hieber, *Ber.*, 1921, 54, [B], 902; *A.*, ii, 466.

⁶⁵ W. Dieckmann, *ibid.*, 2251; *A.*, ii, 716.

⁶⁶ A. Grün and T. Wirth, *Z. Deut. Oel-Fett Ind.*, 1921, 41, 145; *A.*, ii, 660.

⁶⁷ A. Lachman, *J. Ind. Eng. Chem.*, 1921, 13, 230; *A.*, ii, 355.

⁶⁸ H. Yanagisawa, *J. Pharm. Soc. Japan*, 1921, 240; *A.*, ii, 418.

⁶⁹ P. H. Hermans, *Chem. Weekblad*, 1921, 18, 348; *A.*, ii, 467.

⁷⁰ A. Heiduschka and F. Englert, *Z. anal. Chem.*, 1921, 60, 161; *A.*, ii, 524.

⁷¹ E. Schulek, *Pharm. Zentr.-h.*, 1921, 62, 391; *A.*, ii, 603.

values of a fat before and after acetylation has been worked out,⁷² and a more exact method of separating solid from liquid fatty acids in the form of their lead salts has been devised.⁷³

The conditions under which cholesterol and allied substances may be accurately estimated have been studied, and the colorimetric method has been shown to be inapplicable to the unsaponifiable matter of fæces.⁷⁴

A new measure for the activity of amylase solutions has been recommended as giving more absolute values— $Sf = K \times \text{maltose (in grams)}/\text{enzyme preparation (grams)}$, where K represents the constant of the unimolecular reaction during the first part of the hydrolysis.⁷⁵

In using taka diastase for the estimation of starch, the results vary with the origin of the enzymic preparation, and it is therefore necessary to make control experiments on pure starch with each enzyme.⁷⁶

An iodometric method of estimating the diastatic capacity of malt has been based on the oxidation of the resulting maltose to maltobionic acid by means of an alkaline solution of iodine, the amount of iodine required affording a measure of the maltose.⁷⁷

The conditions under which dextrose is quantitatively oxidised by alkaline permanganate have also been ascertained and adapted to the estimation of starch and dextrose,⁷⁸ and the same principle has also been used for the estimation of lactose.⁷⁹

Lævulose, like other sugars and polyhydric alcohols, combines with boric acid to form an acid compound, and the proportion of boric acid entering into combination affords a means of estimating that sugar.⁸⁰

A new volumetric method of estimating reducing sugars involves the use of an alkaline solution of potassium ferricyanide standardised against pure dextrose.⁸¹ The process may be used for the estimation of dextrose formed in the hydrolysis of certain glucosides.⁸²

⁷² E. André, *Compt. rend.*, 1921, **172**, 984; *A.*, ii, 419.

⁷³ E. Twitchell, *J. Ind. Eng. Chem.*, 1921, **13**, 806; *A.*, ii, 662.

⁷⁴ J. A. Gardner and M. Williams, *Biochem. J.*, 1921, **15**, 363, 376; *A.*, ii, 563.

⁷⁵ H. von Euler and O. Svanberg, *Z. physiol. Chem.*, 1921, **112**, 193; *A.*, ii, 528.

⁷⁶ E. Horton, *J. Agric. Sci.*, 1921, **11**, 240; *A.*, ii, 661.

⁷⁷ J. L. Baker and H. F. E. Hulton, *Analyst*, 1921, **46**, 90; *A.*, ii, 420.

⁷⁸ F. A. Quisumbing, *Philippine J. Sci.*, 1920, **16**, 581; *A.*, ii, 67.

⁷⁹ F. T. Adriano, *ibid.*, 1920, **17**, 213; *A.*, ii, 284.

⁸⁰ G. van B. Gilmour, *Analyst*, 1921, **46**, 3; *A.*, ii, 221.

⁸¹ A. Jonescu and V. Vargolici, *Bul. Soc. Chim. România*, 1920, **2**, 38; *A.*, ii, 283.

⁸² A. Jonescu, *ibid.*, 1921, **3**, 6; *A.*, ii, 525.

A colorimetric method of estimating dextrose in urine has been based on the fact that when heated in the presence of sodium carbonate it reduces 4 : 6-dinitroguaiacol to 4-nitro-6-aminoguaiacol, which has an intense colour.⁸³

Another suitable reagent for the colorimetric estimation of dextrose is 3 : 5-dinitrosalicylic acid.⁸⁴

An iodometric method of estimating phenylhydrazine has been devised, and adapted to the estimation of pentosans and pentoses.⁸⁵

Lævulic acid in foods may be estimated by oxidation with dichromate and sulphuric acid, and distillation and titration of the resulting acetic acid. Formic, acetic, and lactic acids must first be separated from the original substance.⁸⁶

For the separation of aliphatic amines, advantage has been taken of the solubility of ammonium chloride and monomethylamine hydrochloride in chloroform. The ammonia may then be separated by treatment with yellow mercuric oxide, whilst trimethylamine may be separated from dimethylamine by converting it into its periodide.⁸⁷

An accurate method of titrating aniline involves diazotisation with standard sodium nitrite solution, potassium iodide-starch paper being used as outside indicator.⁸⁸

Better results are obtained in the titration of certain alkaloids by using bromophenol-blue in place of the usual indicators, whilst methyl-red is the most suitable indicator for quinine hydrogen salts.⁸⁹

Theobromine can be separated in a very pure condition by means of a method in which tetrachloroethane is used for the extraction.⁹⁰

Inorganic Analysis.

Qualitative.—The applications of spot reactions on filter-paper as a preliminary test have been systematised, and attention has been directed to the use of the reactions of aluminium, uranium, and chromium with alizarin colouring matters and of manganese with benzidine.⁹¹

It has been shown that sodium thioantimonate is a useful general

⁸³ J. B. Sumner, *Physiol. Abstr.*, 1921, **6**, 170; *A.*, ii, 526.

⁸⁴ J. B. Sumner and V. A. Graham, *J. Biol. Chem.*, 1921, **47**, 5; *A.*, ii, 564.

⁸⁵ A. R. Ling and R. D. Nanji, *Biochem. J.*, 1921, **15**, 466; *A.*, ii, 601.

⁸⁶ L. Grünhut, *Z. Unters. Nahr. Genussm.*, 1921, **41**, 261; *A.*, ii, 602.

⁸⁷ H. Franzen and A. Schneider, *Biochem. Z.*, 1921, **116**, 195; *A.*, ii, 663.

⁸⁸ T. Sabalitscka and H. Schrader, *Z. anal. Chem.*, 1921, **34**, 45; *A.*, ii, 224.

⁸⁹ N. Evers, *Pharm. J.*, 1921, **106**, 470; *A.*, ii, 527.

⁹⁰ R. V. Wadsworth, *Analyst*, 1921, **46**, 32; *A.*, ii, 225.

⁹¹ F. Feigl and R. Stern, *Z. anal. Chem.*, 1921, **60**, 1; *A.*, ii, 279.

reagent for certain metals. In the case of mercury, the colour of the precipitate varies with the particular salt.⁹²

A delicate test for the hydrides of arsenic, antimony, and phosphorus has been based on the fact that they produce a violet coloration on sodium aurochloride test-paper.⁹³

As little as 0.0000034 gram of gaseous ammonia may be detected by the film-mirror which it produces on a drop of silver nitrate solution containing 3 per cent. of formaldehyde.⁹⁴ Another new test for ammonia depends on its conversion into hexamethylenetetramine picrate, which forms characteristic, microscopic crystals.⁹⁵

Several tests for individual metals will be found useful in systematic analysis. A reaction capable of detecting mercury in a solution of 2 mg. per litre depends on the formation of cuprous mercuric iodide; it is applied in the form of test-paper.⁹⁶

Bettendorff's reagent (stannous chloride in hydrochloric acid) is capable of detecting 0.01 mg. of arsenic trioxide; in the case of dark solutions, the arsenic is first evolved as hydrogen arsenide.⁹⁷

A method of detecting antimony in the presence of tin is based on its precipitation from hydrochloric acid solution as red oxy-sulphide by means of sodium thiosulphate solution, whereas stannic chloride gives a white precipitate of sulphide and hydroxide. Cupric salts must be removed before applying the test.⁹⁸

Aluminium, iron, chromium, and manganese may be detected by the form and colour of their crystalline compounds with salicylic acid.⁹⁹

A new and sensitive reagent for the detection of cobalt is either a nitroso-compound or an oxamino-compound, which is prepared by heating an acidified solution of *R*-salt (sodium β -naphthol-3 : 6-disulphonate) with sodium nitrite. Its aqueous solution forms a green compound with ferrous salts, a brownish-yellow compound with nickel, and a deep red dye with cobalt.¹ Iron and cobalt may also be distinguished from nickel by the colorations given by their salts with dimethylglyoxime solution and ammonia.²

Comparative tests of the sensitiveness of the ordinary reagents for barium ion have shown that sulphuric and chromic acids are

⁹² A. Langhans, *Z. anal. Chem.*, 1921, **60**, 91; *A.*, ii, 353.

⁹³ W. Zimmermann, *Apoth. Ztg.*, 1921, **36**, 29; *A.*, ii, 276.

⁹⁴ C. D. Zenghilis, *Compt. rend.*, 1921, **173**, 153; *A.*, ii, 558.

⁹⁵ C. Collo and V. Teodossiu, *Bul. Soc. Chim. România*, 1920, **2**, 100; *A.*, ii, 214.

⁹⁶ P. Artmann, *Z. anal. Chem.*, 1921, **60**, 81; *A.*, ii, 350.

⁹⁷ L. W. Winkler, *Pharm. Zentr.-h.*, 1921, **62**, 125; *A.*, ii, 275.

⁹⁸ V. Njegovan, *Chem. Ztg.*, 1921, **45**, 681; *A.*, ii, 563.

⁹⁹ C. van Zijp, *Pharm. Weekblad*, 1921, **58**, 694; *A.*, ii, 463.

¹ H. S. van Klooster, *J. Amer. Chem. Soc.*, 1921, **43**, 746; *A.*, ii, 415.

² W. Vaubel, *Z. öfentl. Chem.*, 1921, **27**, 163; *A.*, ii, 596.

the most sensitive (1:1,600,000 and 1:1,200,000) and sodium arsenate the least sensitive (1:175).³

A simple method of detecting sodium and potassium in the presence of magnesium depends on the formation of the compound $K_2CuPb(NO_3)_6$, which crystallises in microscopic, black cubes, and of sodium pyroantimonate, which also has a characteristic microscopic appearance.⁴

The reaction between azoimide and nitrous acid— $HNO_3 + HN_3 = H_2O + N_2O + N_2$ —has been applied to the detection of nitric acid in the presence of nitrous acid, the latter being thus removed before testing for the former.⁵

In applying the diphenylamine test, it is necessary to have a definite concentration of the liquid, and this is best found by adding successive quantities of water.⁶

Quantitative.—Guanidine carbonate, being non-hygroscopic, is a convenient substance to use for the standardisation of acid solutions.⁷ Another original standard, which gives trustworthy results in alkalimetry, is potassium hydrogen oxalate.⁸

Two new forms of apparatus for colorimetric estimations have been devised.⁹

In using cresol-red as indicator in determinations of hydrogen-ion concentration a correction is necessary for the presence of salt.¹⁰ Some indicators are too sensitive for certain estimations, such as the titration of an alkali acetate with an acid; in such cases, tropæolin-O and -OO may be serviceable.¹¹ By using two indicators simultaneously it is possible to titrate many coloured solutions with accuracy,¹² and in some cases, where this method is not applicable, the colouring matter may be bleached with hydrogen peroxide.¹³

When only small amounts of solution are available, indicator papers may be used in presence of a buffer solution.¹⁴

The new indicators described include a compound prepared by

³ O. Lutz, *Z. anal. Chem.*, 1921, **60**, 209; *A.*, ii, 596.

⁴ E. Ludwig and (Mlle) H. Spirescu, *Bul. Soc. Chim. România*, 1920, **2**, 78; *A.*, ii, 215.

⁵ E. Oliveri-Mandalà, *Gazzetta*, 1921, **51**, i, 138; *A.*, ii, 346.

⁶ A. E. Weinhagen, *J. Amer. Chem. Soc.*, 1921, **43**, 685; *A.*, ii, 346.

⁷ A. H. Dodd, *J. Soc. Chem. Ind.*, 1921, **40**, 89T; *A.*, ii, 409.

⁸ Y. Osaka and K. Andô, *J. Tokyo Chem. Soc.*, 1920, **41**, 945; *A.*, ii, 132.

⁹ E. Alstone, *Soil Sci.*, 1920, **10**, 467; *A.*, ii, 214. N. Evers, *Analyst*, 1921, **46**, 392; *A.*, ii, 705.

¹⁰ R. C. Wells, *J. Amer. Chem. Soc.*, 1920, **42**, 2160; *A.*, ii, 55.

¹¹ I. M. Kolthoff, *Z. anorg. Chem.*, 1921, **115**, 168; *A.*, ii, 465.

¹² J. L. Lizius, *Analyst*, 1921, **46**, 355; *A.*, ii, 650.

¹³ C. A. Mitchell, *ibid.*, 131.

¹⁴ I. M. Kolthoff, *Pharm. Weekblad*, 1921, **58**, 961; *A.*, ii, 515.

the interaction of ethyl nitrate and magnesium phenyl bromide,¹⁵ and two new phthaleins, one of which is unaffected by excess of alkali or alcohol; both are available between P_H 8.9 and 10.2.¹⁶

There have been but few additions to the general methods of oxidation or reduction. It has been shown, however, that the addition of manganese sulphate accelerates the reaction between potassium permanganate and hydrogen peroxide or sodium oxalate.¹⁷

A sharp method of titrating arsenious compounds with standard dichromate solution is to add potassium bromide and hydrochloric acid, and to pass a current of air through the liquid. The bromine liberated by the first drop in excess of dichromate is carried over into potassium iodide solution and the liberated iodine indicated by means of starch.¹⁸ An analogous method may be used for the titration of ferrous salts with permanganate solution.¹⁹

An oxidimetric method of estimating manganese in hydrofluoric acid solution by means of potassium permanganate has been shown to give results as accurate as those obtained by other volumetric processes.²⁰

A volumetric method of estimating mixtures of permanganate, dichromate, and chromic salts is based on the fact that permanganate is converted into hydrated manganese dioxide by the action of manganese sulphate and zinc sulphate, whilst dichromate is unaffected. By titrating the liquid with ferrous sulphate solution before and after this treatment, the amounts of the two substances are found.²¹

For the estimation of traces of hydrogen peroxide, ferrous sulphate is used as the reducing agent, and the resulting ferric sulphate estimated colorimetrically.²²

Mention may also be made of a volumetric method of estimating hyposulphite depending on its reducing action on potassium ferricyanide.²³

The use of cadmium has been recommended in place of zinc for the reduction of ferric salts, since it obviates the risk of iron being deposited when insufficient iron is present.²⁴ Quadrivalent titanium is also quantitatively reduced by cadmium, and it is therefore

¹⁵ R. W. Kinkad, *Chem. News*, 1921, **122**, 4; *A.*, ii, 124.

¹⁶ W. Csánzi, *Z. Elektrochem.*, 1921, **27**, 64; *A.*, ii, 270.

¹⁷ P. H. Segnitz, *J. Ind. Eng. Chem.*, 1920, **12**, 1196; *A.*, ii, 125.

¹⁸ R. Meurice, *Ann. Chim. anal.*, 1921, **3**, 85; *A.*, ii, 85.

¹⁹ R. Meurice, *ibid.*, 23; *A.*, ii, 218.

²⁰ J. Holluta and J. Obrist, *Monatsh.*, 1921, **41**, 555; *A.*, ii, 522.

²¹ N. G. Chatterji, *Chem. News*, 1921, **123**, 232; *A.*, ii, 713.

²² F. W. Horst, *Chem. Ztg.*, 1921, **45**, 572; *A.*, ii, 461.

²³ R. Formhals, *ibid.*, 1920, **44**, 869; *A.*, ii, 58.

²⁴ W. D. Treadwell, *Helv. Chim. Acta*, 1921, **4**, 551; *A.*, ii, 523.

possible to estimate iron and titanium simultaneously by first reducing the solution, and then titrating it with permanganate.²⁵

Several new iodometric methods have been published during the year. When titrating an excess of iodine in acid solution with thiosulphate solution, a sharper end-point may be obtained by adding thiosulphate so as to prevent the ionic concentration of the iodine.²⁶

Lead may be accurately estimated as chromate by iodometric estimation of the excess of chromate in the filtrate from the lead chromate.²⁷ For the iodometric estimation of iron it is essential to have definite concentrations of acid and potassium iodide, and a limit for the proportion of iron.²⁸

An iodometric method of estimating chromium in chromite²⁹ has been devised; and new methods of estimating iodides in the presence of iodates,³⁰ and thiosulphates in the presence of sulphites and tetrathionates,³¹ also involve iodometric processes.

Turning next to the methods of separating metals, we find an important investigation of the conditions under which zinc, cadmium, manganese, and silver may be estimated by volatilising their sulphides in a current of dry hydrogen sulphide.³²

The use of hypophosphorous acid in gravimetric analysis has also been studied, and methods have been devised for its use in separating silver from platinum and other metals.³³

Mercuric chloride can be completely volatilised from its solution in a current of hydrogen chloride, and the principle has been adapted to the separation of mercury from copper, cadmium, iron, and other elements.³⁴

Two new volumetric methods of estimating mercury have also been described.³⁵

Gravimetric methods for the estimation of cadmium have been based on its precipitation as sulphide containing sulphate ion,³⁶

²⁵ W. D. Treadwell and A. Rheiner, *loc. cit.*

²⁶ B. Kohler, *Chem. Listy*, 1920, **14**, 137, 195; *A.*, ii, 410.

²⁷ C. W. Simmons, J. R. Gordon, and H. C. Boehmer, *Canad. Chem. J.*, 1920, **4**, 139; *A.*, ii, 63.

²⁸ I. M. Kolthoff, *Pharm. Weekblad*, 1921, **58**, 1510; *A.*, ii, 713.

²⁹ E. Little and J. Costa, *J. Ind. Eng. Chem.*, 1921, **13**, 228; *A.*, ii, 351.

³⁰ V. Thüringer, *Bul. Soc. Chim. România*, 1920, **2**, 73; *A.*, ii, 214.

³¹ A. Kurtenacker and A. Fritsch, *Z. anorg. Chem.*, 1921, **117**, 262; *A.*, ii, 556.

³² L. Moser and A. Schattner, *Chem. Ztg.*, 1921, **45**, 758; *A.*, ii, 558.

³³ L. Moser and T. Kittl, *Z. anal. Chem.*, 1921, **60**, 145; *A.*, ii, 521.

³⁴ W. Strecker and K. Conradt, *Ber.*, 1920, **53**, [B], 2113; *A.*, ii, 64.

³⁵ E. Billmann and K. Thaulow, *Bull. Soc. chim.*, 1921, [iv], **29**, 587; *A.*, ii, 560.

³⁶ L. W. Winkler, *Chem. Ztg.*, 1921, **34**, 383; *A.*, ii, 539.

and on its precipitation as cadmium ammonium phosphate.³⁷ Bismuth may also be accurately estimated as phosphate.³⁸

Small quantities of arsenic may be estimated colorimetrically by comparing the stain produced by arsenic hydride on mercuric chloride paper, with those produced by known amounts of arsenic. The advantage claimed for the method over the Gutzeit process is that the stains are permanent.³⁹

Antimony may be separated from tin by precipitation as sulphide from a strong hydrochloric acid solution at 80°, the tin sulphide remaining in solution at 25°. The addition of ammonium chloride lowers the temperature of precipitation, and the best results are obtained with a definite concentration of hydrochloric acid.⁴⁰

Zinc may be estimated gravimetrically by precipitation as ammonium zinc phosphate,⁴¹ whilst a volumetric method is to precipitate the metal by means of the double thiocyanate of mercury and potassium, and to titrate the filtrate with mercuric nitrate, iron alum being used as indicator.⁴²

In the absence of certain metals, such as copper and zinc, nickel may be estimated in the presence of cobalt by titration with potassium cyanide solution.⁴³

Nickel and cobalt may be separated by simultaneous precipitation as xanthates, and treatment of the precipitate with dilute nitric acid,⁴⁴ which dissolves only the nickel compound.

Cobalt gives a brown coloration with dimethylglyoxime in the presence of mineral acids, and a colorimetric method of estimation has been based on this fact.⁴⁵

A method of separating ferric, aluminium, and chromium hydroxides is to boil the precipitate with 10 per cent. sodium hydroxide solution containing sodium perborate, which dissolves the aluminium and chromium hydroxides.⁴⁶

A new process of estimating iron and manganese depends on

³⁷ L. W. Winkler, *Z. angew. Chem.*, 1921, **34**, 466; *A.*, ii, 656.

³⁸ W. R. Schoeller and E. F. Waterhouse, *Analyst*, 1920, **45**, 435; *A.*, ii, 135.

³⁹ J. Cribier, *J. Pharm. Chim.*, 1921, [vii], 24; *A.*, ii, 653.

⁴⁰ G. Luff, *Chem. Ztg.*, 1921, **45**, 229, 254, 274, 291; *A.*, ii, 353.

⁴¹ L. W. Winkler, *Z. angew. Chem.*, 1921, **34**, 235; *A.*, ii, 521.

⁴² I. M. Kolthoff and C. van Dijk, *Pharm. Weekblad*, 1921, **58**, 538; *A.*, ii, 413.

⁴³ G. H. Stanley, *J. S. African Anal. Chem.*, 1921, **4**, 10; *A.*, ii, 351.

⁴⁴ A. Whitby and J. P. Beardwood, *J. Chem. Met. Soc. S. Africa*, 1921, **21**, 199; *A.*, ii, 562.

⁴⁵ S. A. Bradley and F. B. Hobart, *J. Amer. Chem. Soc.*, 1921, **43**, 482; *A.*, ii, 351.

⁴⁶ (Mme) M. and M. Lemarchands, *Ann. Chim. anal.*, 1921, **3**, 86; *A.*, ii, 351.

their precipitation as hydroxides by means of hexamethylenetetramine.⁴⁷

A method of estimating gallium, in the absence of zinc, is to precipitate it as ferrocyanide, to decompose the precipitate with hydrogen peroxide or sodium hydroxide, and to precipitate the gallium as hydroxide.⁴⁸

Investigation of the methods of separating aluminium from glucinum has shown that accurate results are obtainable by precipitating the metals as hydroxides, dissolving the precipitate in the smallest possible amount of sodium hydroxide solution, and boiling the solution to precipitate the glucinum hydroxide.⁴⁹

Under specified conditions, separation by means of sodium hydrogen carbonate⁵⁰ also gives satisfactory results.⁵¹

Colorimetric methods of estimating small amounts of chromium in steel have been published, one of these being based on the red coloration given by chromic acid with diphenylsemicarbazide solution.⁵²

For the estimation of vanadium in steels and iron alloys precipitation with "cupferron" (the ammonium salt of nitrosophenylhydroxylamine) gives trustworthy results.⁵³ The reagent is also applicable to the separation of zinc from uranium.⁵⁴

A hydrolytic process of separating some of the rare earths by means of creams of insoluble oxides and carbonates has been developed.⁵⁵

It has been shown that the composition of potassium platinumchloride as usually separated does not correspond with the formula K_2PtCl_6 , but that results much closer to the theoretical value may be obtained by precipitating the salt with alcohol, and drying the salt at 110° .⁵⁶

A new method of estimating potassium in silicates by precipitation as perchlorate is available in the absence of sodium and calcium sulphates.⁵⁷ For the estimation of potassium in the presence of sodium and magnesium sulphates and phosphates

⁴⁷ C. Kollo, *Bul. Soc. Chim. România*, 1920, **2**, 89; *A.*, ii, 218.

⁴⁸ L. E. Porter and P. E. Browning, *J. Amer. Chem. Soc.*, 1921, **43**, 111; *A.*, ii, 277.

⁴⁹ H. T. S. Britton, *Analyst*, 1921, **46**, 359; *A.*, ii, 657.

⁵⁰ C. L. Parsons and S. K. Barnes, *J. Amer. Chem. Soc.*, 1906, **28**, 1589; *A.*, 1907, ii, 52.

⁵¹ H. T. S. Britton, *Analyst*, 1921, **46**, 437; *A.*, ii, 712.

⁵² B. S. Evans, *ibid.*, 285; *A.*, ii, 562.

⁵³ L. Rolla and M. Nuti, *Giorn. Chem. Ind. Appl.*, 1921, **3**, 287; *A.*, ii, 597.

⁵⁴ A. Angeletti, *Gazzetta*, 1921, **51**, i, 285; *A.*, ii, 524.

⁵⁵ A. C. Neish and J. W. Burns, *Can. Chem. Met.*, 1921, **5**, 69; *A.*, ii, 560.

⁵⁶ A. Vürtheim, *Chem. Weekblad*, 1920, **17**, 637; *A.*, ii, 61.

⁵⁷ J. J. Morgan, *J. Ind. Eng. Chem.*, 1921, **13**, 225; *A.*, ii, 349.

advantage has been taken of the fact that potassium perchlorate is insoluble in methyl alcohol, whilst sodium and magnesium perchlorates, phosphates, and sulphates are soluble.⁵⁸

Another new method depends on the precipitation of potassium as picrate.⁵⁹

A colorimetric method of estimating traces of bromine has been based on the coloration which it gives with Schiff's reagent.⁶⁰

A new reagent termed "fornitral" (formic acid in combination with *endo*-anilodiphenyldihydrotriazole) gives a quantitative precipitate with nitric acid.⁶¹

Hypochlorites may be rapidly estimated by a gasometric method, which consists in treating them with an alkaline solution of hydrazine and measuring the nitrogen evolved.⁶²

Strychnine forms an insoluble phosphomolybdate, and advantage has been taken of the fact for the estimation of small quantities of phosphoric acid.⁶³ Another method has been based on the formation of a dense yellow liquid, immiscible with water, when phosphoric acid is shaken with ether in the presence of another acid and an alkali molybdate. This yellow liquid is separated by centrifuging and its volume read.⁶⁴

The difference in the solubility of the respective silver salts in 0.5 to 1.5*N*-sodium hydroxide solution affords a means of separating arsenates and arsenites.⁶⁵

Electrochemical Analysis.

A simple apparatus, which can be made in the laboratory, has been devised for the electrometric determination of hydrogen-ion concentration.⁶⁶ Another apparatus has for its aim the measurement of hydrogen-ion concentration without allowing any volatile matter to escape.⁶⁷

The principles applicable to conductivity titrations have been elucidated, and it has been shown that in the case of very weak acids and bases accurate results are obtained only within definite limits for the concentration and dissociation constants. Methods

⁵⁸ H. Atkinson, *Analyst*, 1921, **46**, 354; *A.*, ii, 654.

⁵⁹ St. Minovici and A. Jonescu, *Bul. Soc. Chim. România*, 1921, **3**, 25; *A.*, ii, 520.

⁶⁰ E. Oppenheimer, *Arch. Exp. Path. Pharm.*, 1921, **89**, 17; *A.*, ii, 273.

⁶¹ *Ann. Chim. anal.*, 1921, [ii], **3**, 207; *A.*, ii, 558.

⁶² A. Macbeth, *Chem. News*, 1921, **122**, 268; *A.*, ii, 461.

⁶³ G. Embden, *Z. physiol. Chem.*, 1921, **113**, 138; *A.*, ii, 462.

⁶⁴ H. Copaux, *Compt. rend.*, 1921, **173**, 656; *A.*, ii, 707.

⁶⁵ G. W. Sears, *J. Amer. Chem. Soc.*, 1921, **43**, 466; *A.*, ii, 347.

⁶⁶ G. W. Monier-Williams, *Analyst*, 1921, **46**, 315; *A.*, ii, 650.

⁶⁷ A. B. Hastings, *J. Biol. Chem.*, 1921, **46**, 463; *A.*, ii, 460.

for reducing the dissociation of salts, and for correcting the results where the dissociation limits have been exceeded, have therefore been devised.⁶⁸

The catalytic production of formic acid when the solution in a hydrogen electrode contains carbonates is a probable source of error in electrometric estimations with such electrodes.⁶⁹

The low results obtained in the electrolytic deposition of mercury have been investigated, and the conditions for accurate estimation determined. When the cyanide method is used, it is essential that the current should not be too strong, and that a large amount of potassium cyanide should not be present.⁷⁰

When a silver cathode is used for the electro-deposition of copper, the deposit may be readily removed by means of an ammoniacal solution of ammonium trichloroacetate. This dissolves copper, cadmium, and zinc readily, and nickel slightly, but does not dissolve silver.⁷¹

The conditions under which copper can be electrolytically estimated in solutions also containing arsenic, antimony, bismuth, selenium, and molybdenum have been investigated. As a rule, deposition of the metals only begins after the bulk of the copper has separated, but selenium and tellurium are deposited at the beginning of the electrolysis. Various reagents must therefore be employed.⁷²

For the separation of mercury and copper in the presence of chlorine ions, the solution is electrolysed at a voltage of 2.2 and a relatively low amperage, and after deposition of the mercury the voltage and amperage are increased.⁷³

A modified method for the electrolytic separation of copper, antimony, and tin has also been devised.⁷⁴

For the rapid separation of gold from copper, palladium, and platinum advantage has been taken of the fact that it is quantitatively deposited from a solution of its chloride containing acetate.⁷⁵

Vanadium, tungsten, molybdenum, ferrous salts, chromates, and tartrates interfere with the electrolytic estimation of cobalt and nickel in cobalt steels, and a method for the removal of these substances has been worked out.⁷⁶

⁶⁸ I. M. Kolthoff, *Chem. Weekblad*, 1920, **17**, 694; *A.*, ii, 124.

⁶⁹ C. L. Evans, *J. Physiol.*, 1920, **54**, 353; *A.*, ii, 271.

⁷⁰ W. Böttger, *Z. Elektrochem.*, 1920, **26**, 445; *A.*, ii, 65.

⁷¹ H. Waters, *J. Amer. Chem. Soc.*, 1921, **43**, 700; *A.*, ii, 414.

⁷² F. G. Hawley, *Eng. and Min. J.*, 1920, **110**, 162; *A.*, ii, 216.

⁷³ W. Böttger, *Z. angew. Chem.*, 1921, **34**, 120; *A.*, ii, 351.

⁷⁴ F. Foerster and D. Aanensen, *Z. Elektrochem.*, 1921, **27**, 10; *A.*, ii, 350.

⁷⁵ W. D. Treadwell, *Helv. Chim. Acta*, 1921, **4**, 364; *A.*, ii, 416.

⁷⁶ G. E. F. Lundell and J. F. Hoffmann, *J. Ind. Eng. Chem.*, 1921, **13**, 540; *A.*, ii, 561.

An accurate method of estimating cobalt is to precipitate it with nitroso- β -naphthol, to ignite the precipitate, and fuse it with alkali sulphate, and to electrolyse the solution after the addition of ammonia and ammonium chloride.⁷⁷

Iodides may be titrated with permanganate in presence of free sulphuric acid, by means of the potentiometer, provided that the concentration of the acid is not less than 0.13*N*.⁷⁸ The method may also be used as a standard in oxidimetry,⁷⁹ and analogous methods have been devised for the electrometric estimation of bromates, dichromates, nitrites, and chlorides.⁸⁰

In the case of iodates, reduction is first effected by adding an excess of standard iodide solution in dilute sulphuric acid, and the excess is electrometrically titrated with potassium permanganate. Conversely, an iodide may be titrated with an iodate, and silver may be estimated by titration with iodide and potassium permanganate solution.⁸¹

The electrometric method also enables sharp results to be obtained in the titration of hypochlorous acid with arsenious acid or with potassium iodide.⁸²

Water Analysis.

The usual turbidity standard used in the analysis of waters, which is based on an optical measurement, has been shown to be untrustworthy, and in order to eliminate the error, which in some cases is as great as 50 per cent., the use of a standard powdered silica with particles of uniform size is suggested.⁸³

Sulphuric acid in water may be rapidly estimated by measuring the time required for the first indications of turbidity to appear after the addition of acidified barium chloride solution under standard conditions. In estimating sulphuric acid gravimetrically, it is essential that calcium should first be removed.⁸⁴

The results of further work on the estimation of active carbon dioxide in water⁸⁵ have shown that the table of Tillmans and Heublein for the solubility product of calcium carbonate in the presence of carbon dioxide is inaccurate.

⁷⁷ K. Wagenmann, *Metall u. Erz.*, 1921, **18**, 447; *A.*, ii, 658.

⁷⁸ I. M. Kolthoff, *Rec. trav. chim.*, 1921, **40**, 532; *A.*, ii, 555.

⁷⁹ W. S. Hendrixson, *J. Amer. Chem. Soc.*, 1921, **43**, 14; *A.*, ii, 273.

⁸⁰ *Idem, ibid.*, 1309; *A.*, ii, 651.

⁸¹ *Idem, ibid.*, 858; *A.*, ii, 411.

⁸² W. D. Treadwell, *Helv. Chim. Acta*, 1921, **4**, 396; *A.*, ii, 410.

⁸³ *Bureau of Standards, Sci. Paper*, No. 367, 1920; *A.*, ii, 56.

⁸⁴ L. W. Winkler, *Z. angew. Chem.*, 1920, **33**, 311; *A.*, ii, 126.

⁸⁵ Compare *Ann. Reports*, 1920, **17**, 150.

A new table has therefore been calculated for active carbon dioxide based on the equation—

$$[\text{CO}_2] = (\alpha^3[\text{HCO}_3]'^2 \cdot \frac{1}{2}[\text{Ca}^{**}]) / (1.13 \times 10^{-4}),$$

and is applicable when the concentrations of HCO_3' , CO_2 , and $[\text{Ca}^{**}]$ are known.⁸⁶

The total carbon dioxide content of water may be conveniently calculated from the results of the colorimetric determination of the hydrogen-ion concentration, with neutral-red as indicator, and the estimation of the hydrogen carbonate content.⁸⁷

A rapid colorimetric method of estimating phosphates in water has been based on the formation of a blue coloration when a dilute solution of phosphoric acid is treated with a sulphuric acid solution of ammonium molybdate in the presence of stannous chloride.⁸⁸

A valuable addition to the criteria of the purity of water consists in testing for indican, the presence of even a trace of which may be regarded as an indication of pollution with animal excretions. The test is based on the conversion of the indican into a red or bluish-violet indolignone colouring matter, which can be extracted with chloroform. Nitrites, however, interfere with the reaction and must be removed before applying the test.⁸⁹

For the estimation of hydrogen sulphide in natural waters, carbonates must first be removed by means of barium chloride, and the filtrate treated with standard iodine solution, followed by an excess of standard thiosulphate solution, and the excess titrated with iodine solution.⁹⁰ A method of estimating volatile hydrogen sulphide and carbon dioxide as hydrogen carbonate in mineral sulphide water consists in boiling the water in a current of hydrogen, and absorbing the hydrogen sulphide and carbon dioxide in an ammoniacal solution of cadmium chloride and barium chloride. On acidifying this solution with acetic acid, the cadmium sulphide remains, whilst the carbon dioxide is liberated and absorbed in the usual manner.⁹¹

Reference may also be made to a new form of soap solution for estimating the hardness of water. This is prepared by neutralising a solution of palmitic or oleic acid in propyl alcohol with sodium hydroxide.⁹²

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⁸⁶ I. M. Kolthoff, *Chem. Weekblad*, 1920, **17**, 390; *A.*, ii, 60.

⁸⁷ *Idem*, *Z. Nahr. Genussm.*, 1921, **41**, 112; *A.*, ii, 409.

⁸⁸ D. Florentin, *Ann. Chim. anal.*, 1921, **3**, 295.

⁸⁹ A. Jolles, *Ber. Deut. Pharm. Ges.*, 1920, **30**, 421; *A.*, ii, 69.

⁹⁰ É. Chrétien and H. Vandenberghé, *Ann. Chim. anal.*, 1921, [ii], **3**, 19; *A.*, ii, 214.

⁹¹ J. G. Fairchild, *J. Washington Acad. Sci.*, 1920, **10**, 559; *A.*, ii, 126.

⁹² L. W. Winkler, *Z. angew. Chem.*, 1920, **34**, 143; *A.*, ii, 413.

PHYSIOLOGICAL CHEMISTRY.

LAST year the death of Wilhelm Pfeffer was recorded; now we regret that of his most prominent pupil, Friedrich Czapek, who had succeeded him as Professor of Botany at Leipzig. Czapek was best known to biochemists through his monumental "*Biochemie der Pflanzen*," of which the second edition was completed in 1921 by the publication of the third volume. We have further to record the death of Oswald Schmiedeberg, who during the tenure of his chair at Strassburg (1872-1918) trained many of the pharmacologists of to-day. Apart from pharmacology, Schmiedeberg was much interested in physiological chemistry; his most important contribution to this subject was probably his work on chondroitin-sulphuric acid.

It is perhaps no matter for regret that no new journals of biochemical importance have been started during the current year. The outstanding publication, at least as regards size, is the "*Handbuch der biologischen Arbeitsmethoden*," edited by E. Abderhalden. At the time of writing, more than fifty parts have appeared, on subjects ranging from the preparation of laboratory reagents to the psychology of religion. The work therefore covers a larger field than the "*Biochemische Arbeitsmethoden*," which it is designed to replace. Whilst parts are excellent, in a compilation by 500 contributors the maintenance of a uniform standard cannot be expected, and biochemists who peruse the work will perhaps not always escape a feeling of disappointment, or possibly of irritation.

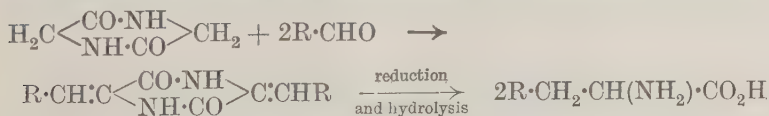
Until recently, there were but few original text-books of biochemistry or chemical physiology in English. This year three new ones have appeared, of unequal scope and merit: "*Principles of Biochemistry*," by Brailsford Robertson, "*Biological Chemistry*," by H. E. Roaf, and "*Biochemistry*," by B. Moore. The first-named book deals fully with most aspects of descriptive and dynamic biochemistry, and its value to the advanced student is increased by a select bibliography to each chapter. The second book is of a more elementary character. The third is largely reprinted from original papers by the author; in spite of its title, it only deals with a small portion of the subject. Biochemistry seems as yet too young to have evolved a standard type of text-book. A comparison of English and foreign books on the subject shows a greater disproportion in the treatment of various sub-

divisions than is met with among text-books of organic chemistry, for instance. But possibly this lack of uniformity is inherent in the science, or in its relation to physiology. The increased interest in biochemistry in this country is not only shown by the publication of new text-books; the subject was much in evidence at the Edinburgh meeting of the British Association.

Of other new books published in 1921, the following may be mentioned: "Applied Colloid Chemistry, General Theory," by W. D. Bancroft; "The Chemistry of Enzyme Action," by K. G. Falk; "Vitamines. Essential Food Factors," by B. Harrow (elementary and semi-popular); "Praktikum der physikalischen Chemie, insbesondere der Kolloidchemie, für Mediziner und Biologen," by L. Michaelis; "Practical Chemical Analysis of Blood," by V. C. Myers (clinical methods); "Organic Medicinal Chemicals," by M. Barrowcliff and F. H. Carr (a practical book concerned with manufacture), and "Organic Compounds of Mercury," by F. C. Whitmore. Nearly all these are American. A second edition of Pfeffer's "Osmotische Untersuchungen" (a reprint) has appeared after a lapse of forty-four years. Attention may be directed to three articles of chemical interest which have appeared in *Physiological Reviews*: "The Carbon Dioxide Carriers of the Blood," by D. D. van Slyke (1921, **1**, 141—176); "The Sugar of the Blood," by J. J. R. Macleod (pp. 208—233); and "Physiological Oxidations," by H. D. Dakin (pp. 394—420). Finally, we may perhaps mention here a new development, which may prove of great convenience to research workers; the firm of Hoffmann-Laroche and Co. has published a catalogue ("Produits biochimiques," Roche) of pure substances of biochemical importance, which they are putting on the market; the list comprises amino-acids, proteins, and substances like acetylcholine, colamine, etc., which have not hitherto been obtainable commercially.

Amino-acids and Proteins.

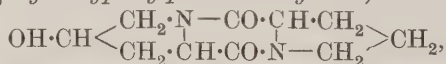
A new general method for synthesising amino-acids, or rather a modification of the well-known Erlenmeyer method, has been described by T. Sasaki,¹ who finds that aldehydes can be condensed with glycine anhydride (diketopiperazine), which replaces the hippuric acid used by Erlenmeyer. Its condensation product



¹ *Ber.*, 1921, **54**, [B], 163, 2056; *A.*, i, 196, 808,

with two molecules of aldehyde is readily reduced to the anhydride of a new amino-acid, which is hydrolysed more easily to the amino-acid itself than when hippuric acid is employed. In this way, phenylalanine, tyrosine, dihydroxyphenylalanine, etc., have been prepared, generally in good yield. Mixed anhydrides of glycine and another amino-acid condense with only one aldehyde molecule.² Thus *dl*-leucylglycine anhydride, when heated with benzaldehyde, sodium acetate, and acetic anhydride, yields the substance $C_4H_9 \cdot CH < \begin{smallmatrix} NAc \cdot CO \\ CO - NH \end{smallmatrix} > C : CHPh$, which, by reduction and hydrolysis, should furnish leucylphenylalanine anhydride and a corresponding dipeptide. Unfortunately, extensive racemisation occurs; otherwise this would constitute a valuable method for preparing some of the less accessible dipeptides.

The hydrolysis of gelatin by acids has been studied exhaustively by H. D. Dakin³ with his new butyl alcohol method;⁴ 91.3 per cent. of the protein was isolated as pure amino-acids. It is interesting to compare Dakin's results with those of the first use of the ester method, by Fischer, Levene, and Aders, in 1902. These authors found 16.5 per cent. of glycine, 0.8 per cent. of alanine, 2.1 per cent. of leucine, and 5.2 per cent. of proline; Dakin's figures are respectively 25.5, 8.7, 7.1, and 9.5. Yet Dakin found no new amino-acid in gelatin, indeed one less than Fischer and his co-workers, for valine seems to be absent. A new tricyclic peptide was isolated, *γ-hydroxyprolylproline anhydride*,



and unidentified sulphur compounds are also present.

A simple new method for the determination of amino-acids has been indicated by R. Willstätter and E. Waldschmidt-Leitz.⁵ Their carboxyl groups can be titrated in 97 per cent. alcohol with potassium hydroxide and phenolphthalein as indicator. Similarly, polypeptides can be titrated, even if the alcohol is only 40 per cent.

A curious observation on colostrum has been made by P. E. Howe.⁶ The blood of the new-born calf contains neither euglobulin nor pseudo-globulin I, but after it has received colostrum (which is rich in globulin, whereas milk contains scarcely any), the blood contains these two proteins in relatively large amounts. It would appear that the calf receives its first supply of the globulins from the colostrum; if this is withheld, the globulins are only

² T. Sasaki and T. Hashimoto, *Ber.*, 1921, **54**, [B], 168; *A.*, i, 197.

³ *J. Biol. Chem.*, 1920, **44**, 499; *A.*, i, 66.

⁴ *Ann. Reports*, 1919, **16**, 153.

⁵ *Ber.*, 1921, **54**, [B], 2988.

⁶ *J. Biol. Chem.*, 1921, **49**, 115; *A.*, 1922, i, 80.

slowly formed. These observations raise some questions relating to protein assimilation.

J. H. Northrop⁷ has compared the hydrolysis of gelatin by pepsin, trypsin, and alkali with a view to determine which linkings are split by each reagent. Those split by the enzymes are also readily split by alkali, but not by acid. Those split by pepsin are also split by trypsin more slowly, but trypsin splits, in addition, other linkings which are not attacked by pepsin. Naturally, the results are somewhat general in character; they are based on the results of formol titration after hydrolysis by one reagent, or by several reagents in succession.

Polysaccharides.

Judging from the numerous publications of last year, the polysaccharides are being more actively investigated than ever before. The interest is shifting from physiological to organic chemistry, and details must be sought in another division of this Report. Here only a few general points can be dealt with. It should be remembered that the first crystalline degradation products of starch, of greater complexity than maltose, were obtained by a biological agent, Schardinger's *Bacillus macerans*.⁸

These crystalline dextrans were investigated by H. Pringsheim,⁹ first with A. Langhans and then with F. Eissler; they are di-, tri-, tetra-, and hexa-amyloses, and the molecular weight of their acetyl derivatives in a variety of solvents was found to correspond with the formula $(C_6H_{10}O_5)_n$, where n is respectively 2, 3, 4, or 6. These amyloses give green or reddish-brown, crystalline iodine additive compounds, which dissolve to dark red solutions, and they are not attacked by diastase, saliva, pancreatin, or emulsin, but are hydrolysed by takadiastase and *Penicillium africanum*. It now appears, according to the work of P. Karrer and C. Nägeli,¹⁰ that diamylose is simply an anhydride of maltose, and that methylated starch $\{C_6H_8O_3(OMe)_2\}_x$ has a molecular weight of at most 1200. The aqueous solution of this substance shows the Tyndall effect, but after ultra-filtration with little loss it is optically empty and truly crystalloidal. The conclusion is drawn that the starch molecule contains not more than six dextrose residues united by chemically normal linkings, that is, that it is hexa-amylose polymerised by subsidiary valencies; and that it is related to the amylose as a crystal is to a single molecule. H. Pringsheim

⁷ *J. gen. Physiol.*, 1921, **4**, 57; *A.*, i, 823.

⁸ *Ann. Reports*, 1912, **9**, 98.

⁹ *Ber.*, 1912, **45**, 2533; 1913, **46**, 2959; *A.*, 1912, i, 832; 1913, i, 1156.

¹⁰ *Helv. Chim. Acta*, 1921, **4**, 169, 185, 263; *A.*, i, 310, 311, 313.

and W. Persch¹¹ conclude (from a study of tetra-amylose) that the methylation of two hydroxyl groups per hexose residue does not cause depolymerisation, which gives additional significance to the molecular weight determinations of the methylation products. Glycogen is also a polymerised amylose, differing from starch in the degree of polymerisation. Karrer and Nägeli believe the molecular weight of starch to be much smaller than it has been supposed to be by various authors, for instance, M. Samec and H. Haerdtl,¹² who have recorded enormous molecular weights for different varieties of starch, up to 260,000.

Inulin is also a relatively simple substance. H. Pringsheim and A. Aronowsky¹³ find for the molecular weight of triacetyl-inulin in naphthalene, glacial acetic acid, and phenol a mean value of 2633 corresponding with nine fructose residues, and in agreement with this, P. Karrer and L. Lang¹⁴ deduce from the molecular weight of trimethylinulin that there are eight to ten such residues.

The case of cellulose is complicated by the formation of both cellobiose and dextrose on hydrolysis; one of the questions at issue is the amount of the former sugar present in the molecule. Here, as in the case of other polysaccharides, much may be expected from an application of the methylation methods, which have given Irvine and his pupils such valuable results in the case of the disaccharides.

Nucleic Acids.

A second edition of W. Jones's monograph on this subject has appeared, and H. Morel¹⁵ has also published a useful review dealing with it. Both thymus- and yeast-nucleic acid consist of four nucleotides, each composed of phosphoric acid, sugar, and a base, and the main problem remaining is to determine the way in which these four nucleotides are united by loss of three molecules of water. Until recently, Kossel's suggestion was accepted, that the union is through the phosphoric acid groups. On this view, the nucleic acids would be derivatives of a complex pyrophosphoric acid, that is, acid anhydrides. Levene now considers the union to be between phosphoric acid of one nucleotide and the sugar of another, which would make them esters. Jones, whose views have to some extent been adopted by Thannhauser, imagines

¹¹ *Ber.*, 1921, **54**, [B], 3162.

¹² *Koll. Chem. Beihefte*, 1920, **12**, 281; *A.*, 1921, i, 226.

¹³ *Ber.*, 1921, **54**, [B], 1281; *A.*, 1921, i, 545.

¹⁴ *Helv. Chim. Acta*, 1921, **4**, 249; *A.*, i, 312.

¹⁵ *Bull. Soc. chim. Biol.*, 1921, **3**, 176.

anhydride formation between the sugar complexes only; hence he regards the nucleic acids as ethers. As there seems to be no way of attacking this problem by synthesis, the experimental work has been mainly concerned with the products obtained by mild hydrolysis, and the rate at which these products are formed. Heating with dilute ammonia is the method most frequently employed, but picric acid,¹⁶ calcium hydrogen sulphite,¹⁷ boiled pancreatic extract,¹⁸ and snake venom¹⁵ have also been used.

In the case of thymus-nucleic acid, the first argument against a linking between the phosphoric acid groups was advanced by P. A. Levene and W. A. Jacobs,¹⁹ who by hydrolysis with 2 per cent. sulphuric acid were able to split off the two purine derivatives, adenine and guanine; the hexose groups to which these bases are attached are also removed, as lævulic acid. The pyrimidine bases are more firmly held and are each obtained attached to one sugar and *two* phosphoric acid groups, as hexocytidine- and hexothymidine-diphosphoric acids, which give barium salts having respectively the formulæ $C_{10}H_{13}O_{12}N_3P_2Ba_2$ and $C_{11}H_{14}O_{13}N_2P_2Ba_2$; these acids have therefore each four acidic hydrogen atoms. Each phosphoric acid grouping must have two free hydroxyl groups and is united to the sugar by its third hydroxyl. If the two phosphoric acid groups were united together, and one were attached to the sugar, three hydroxyl groups would be used up in anhydride formation and only three would be left, so that the diphosphoric acids isolated by Levene and Jacobs would be tribasic instead of tetrabasic. The same acids have been obtained more recently by S. J. Thannhauser and B. Ottenstein,¹⁶ who consider, however, that they are not preformed in thymus-nucleic acid.

Similar arguments have been adduced against the pyrophosphoric acid formula for yeast-nucleic acid. W. Jones²⁰ has lately attempted to disprove it in another way, by comparing the rates at which phosphoric acid is set free from yeast-nucleic acid and from its four constituent nucleotides. For the entire acid, this rate corresponds with the composite rate calculated for a mixture of the four nucleotides, so that in the formation of these nucleotides by hydrolysis no phosphoric acid group is disturbed. Adenine and guanine are moreover split off from their respective nucleo-

¹⁵ *Bull. Soc. chim. Biol.*, 1921, 3, 176.

¹⁶ S. J. Thannhauser and B. Ottenstein, *Z. physiol. Chem.*, 1921, 114, 39; *A.*, i, 521.

¹⁷ H. Steudel and E. Peiser, *ibid.*, 1920, 111, 297; *A.*, i, 136.

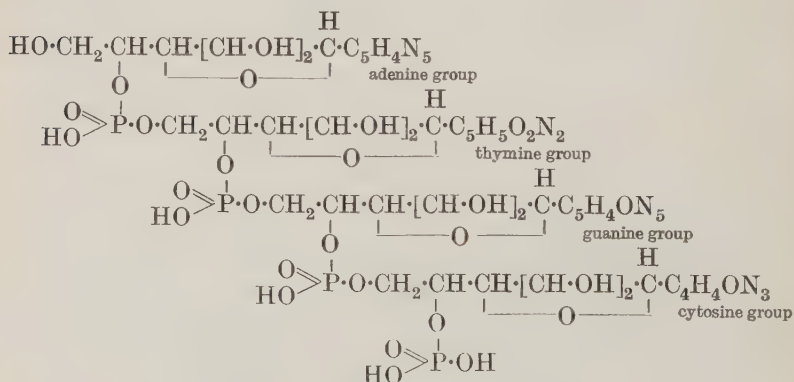
¹⁸ W. Jones, *Amer. J. Physiol.*, 1920, 52, 203; *A.*, 1920, i, 687.

¹⁹ *J. Biol. Chem.*, 1912, 12, 411; *A.*, 1912, i, 926.

²⁰ *Amer. J. Physiol.*, 1920, 52, 193, 203; *A.*, 1920, i, 687.

tides with equal rapidity, so that the linking cannot be through the purine groups, and by a process of elimination Jones draws the conclusion that the four nucleotides are held together through their sugar complexes. Jones further hydrolysed yeast-nucleic acid with boiled extract of pig's pancreas (which does not contain any active agents other than that hydrolysing yeast-nucleic acid; hence it leaves the thymus acid unaffected). He observed not the slightest increase in acidity, which ought to have occurred if an ester grouping had been broken down, and hence he concludes that the union of the nucleotides is between two sugar groups, that is, yeast-nucleic acid is an ether.

Levene, on the other hand, adheres to the ester linking between the phosphoric acid of one nucleotide and the sugar grouping of another. He²¹ considers this to be supported by Jones's experiments on the rate of hydrolysis, which, in his opinion, merely indicate that the union of the four nucleotides is more labile than that between the phosphoric acid and (its own) sugar. The increase in acidity due to the breakdown of the ester grouping does not show itself owing to buffer effect. He formulates thymus-nucleic acid as follows :

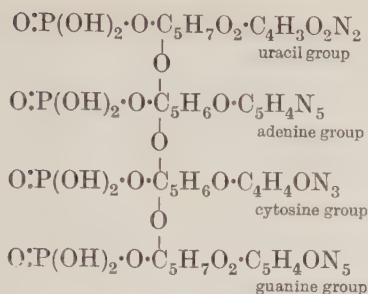


The arrangement of the basic groups is, of course, to some extent arbitrary, but as thymine and cytosine can be obtained with one sugar and two phosphoric acid groups attached (see above), they cannot both be in the same half of the molecule. Levene has given a similar formula for yeast-nucleic acid.²² By way of comparison Jones's formula²³ for this acid may be given.

²¹ *J. Biol. Chem.*, 1921, **48**, 119; *A.*, i, 821.

²² *Ibid.*, 1919, 40, 415; *A.*, 1920, i, 193.

²³ *Amer. J. Physiol.*, 1920, **52**, 203; *A.*, 1920, i, 687.



Finally, we may indicate the present position of the chemical technique of this subject. All the four nucleotides constituting yeast-nucleic acid have been crystallised in the free state;²⁴ their salts are more readily obtained crystalline. In the case of thymus-nucleic acid, the labile attachment of the purine groups and the instability of their hexose residues have prevented the same result from being obtained. Here the furthest advance is marked by the barium salt of hexothymidine-diphosphoric acid, the most complex degradation product of nucleic acid which has so far been crystallised. Alleged di- and tri-nucleotides²⁵ have on further investigation proved to be mixtures of mono-nucleotides.²⁶

Ferments and Fermentation.

Various investigators have at different times suggested that ferment action is preceded by the formation of a complex with the substrate, which formation may require the presence of electrolytes. That this is so in the case of amylase has recently been shown by L. Ambard²⁷ in a paper of considerable interest. Powdered starch removes amylase from solution and keeps it fixed, in spite of repeated washing in the centrifuge. On the other hand, it gives up the ferment promptly to filtered starch and to glycogen solutions containing neutral salt; the latter process the author terms "défixation." It furnishes a convenient method for estimating amylase (in saliva, blood, urine, etc.); 96—100 per cent. of the ferment in a solution may be removed by starch

²⁴ P. A. Levene, *J. Biol. Chem.*, 1920, **41**, 483; *A.*, 1920, i, 452.

²⁵ P. A. Levene and W. A. Jacobs, *ibid.*, 1912, **12**, 411; *A.*, 1912, i, 926. W. Jones and H. C. Germann, *ibid.*, 1916, **25**, 93; *A.*, 1916, i, 515. S. J. Thannhauser and G. Dorfmueller, *Z. physiol. Chem.*, 1917, **100**, 121; *A.*, 1918, i, 47.

²⁶ Compare, respectively, P. A. Levene, *J. Biol. Chem.*, 1921, **48**, 119; *A.*, i, 821. W. Jones and A. F. Abt, *Amer. J. Physiol.*, 1920, **50**, 574; *A.*, 1920, i, 687. P. A. Levene, *J. Biol. Chem.*, 1920, **43**, 379; *A.*, 1920, i, 774.

²⁷ *Bull. Soc. chim. Biol.*, 1921, **3**, 51; *A.*, i, 368.

powder, which is then mixed with filtered starch solution containing sodium chloride and a phosphate mixture (to maintain the optimal P_H 6.6). After keeping at 35° for a time, during which at most one-tenth of the starch is hydrolysed (and the rate is still constant), the action is stopped by alkali, and the maltose is estimated by Bertrand's process. Whether solid starch requires salt for the fixation of amylase could not be established, for the solid starch cannot be washed free from salt. Salt-free glycogen "defixes" only 4 per cent., but on addition of salt, 98 per cent. The change of P_H to 5.0 or to 8.0 had no effect on defixation, but caused in either case a fall of 40 per cent. in the rate of hydrolysis, which is due only to a very slight extent to destruction of the ferment.

The effect of various salts on diastase action has been often investigated, recently again by W. Biedermann,²⁸ who calls the salt a co-ferment and finds that the effect of the anion predominates; sodium chloride is the most active, followed closely by potassium thiocyanate. Nitrates, iodides, and sulphates are much less active; evidently the effect is a lyotropic one. A. Hahn and R. Michalik²⁹ consider, in the case of pancreatic diastase, that the activation by salts is a diminution in the size of the colloidal enzyme particles.

Something similar to Ambard's "défixation" had been observed before in the case of invertase adsorbed on ferric hydroxide, which O. Meyerhof³⁰ found to be as active in a sucrose solution as the same amount of unadsorbed ferment. E. G. Griffin and J. M. Nelson³¹ showed the same to be true when charcoal is the adsorbent; it is only necessary to maintain the proper hydrogen-ion concentration, which is upset by charcoal (this point had been neglected in earlier experiments, by Eriksson on invertase, and by Hedin on rennet). Lately, L. Michaelis³² has described a quantitative confirmation of Meyerhof's experiments, in an interesting paper dealing with the theory of invertase action. Invertase adsorbed on ferric hydroxide cannot be removed by washing with water; it is slowly removed by sucrose, maltose, and raffinose solutions, but not by lactose, dextrose, fructose, mannose, or α - or β -methylglucoside. Although invertase adsorbed on ferric hydroxide is evidently colloidal, Michaelis concludes that the kinetics of a homogeneous system still hold good. The adsorbed invertase

²⁸ *Fermentforsch.*, 1920—1921, **4**, 258; *A.*, i, 468.

²⁹ *Z. Biol.*, 1921, **73**, 10; *A.*, i, 282.

³⁰ *Pflüger's Archiv*, 1914, **157**, 251; *A.*, 1914, ii, 450.

³¹ *J. Amer. Chem. Soc.*, 1916, **38**, 722, 1109; *A.*, 1916, i, 439, 516.

³² *Biochem. Z.*, 1921, **115**, 269; *A.*, i, 468.

molecules must all be on the surface of the ferric hydroxide, and are equally active.

The adsorption of invertase by various reagents has recently been utilised by R. Willstätter and F. Racke³³ for the purification of the enzyme. This work is part of an important investigation of enzymes, begun by Willstätter with a view to their preparation in as pure a state as possible.

The extraction of invertase from yeast by digestion with water is by no means a purely physical process; preliminary autolysis is apparently necessary. The manner in which the yeast has been dried and the addition of antiseptics both affect the process. The crude extract is purified by adding a limited amount of kaolin, which principally adsorbs impurities. The invertase is then adsorbed on aluminium hydroxide, from which it cannot be removed by water, but almost quantitatively by 1 per cent. aqueous disodium hydrogen phosphate, 0.04 per cent. aqueous ammonia, very dilute sodium carbonate, or aqueous pyridine. Invertase decomposes spontaneously in aqueous solution and becomes quite inactive in a year and a half. Previously Willstätter³⁴ had investigated peroxydases. A feature of the extraction of the latter from horse-radish is the prolonged intensive dialysis of thin slices of the root, which is subsequently killed by dilute oxalic acid, and thus the enzyme is set free from the cells. After concentration of the extract, the peroxydase is precipitated by alcohol. In order to control the various operations, a method of estimation has been worked out, depending on the amount of purpurogallin formed (ascertained colorimetrically). After precipitation by alcohol and purification by mercuric chloride, the best specimens were about 2500 times as active as powdered horse-radish. Later, by adsorption on aluminium hydroxide from 50 per cent. alcohol, and recovery by extraction with water containing carbonic acid, the activity of the preparation was nearly doubled. The purest specimens seem to consist chiefly of a nitrogenous glucoside containing more than 30 per cent. of a pentose and an equimolecular proportion of a hexose, with three atomic proportions of nitrogen.

L. Michaelis and M. Rothstein³⁵ have investigated the rate of destruction of rennet and pepsin at various temperatures by different hydroxyl-ion concentrations. Under all conditions, the rate for the two enzymes is in constant proportion. The rate of

³³ *Annalen*, 1921, **425**, 1; *A.*, i, 823.

³⁴ R. Willstätter and A. Stoll, *ibid.*, 1918, **416**, 21; *A.*, 1918, i, 555.
R. Willstätter, *ibid.*, 1921, **422**, 47; *A.*, i, 138.

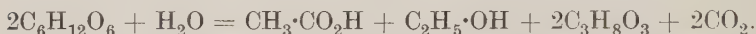
³⁵ *Biochem. Z.*, 1920, **105**, 60; *A.*, 1920, i, 775.

destruction is proportional to the 1.5th power of the amount of enzyme present and to the fourth power of the hydroxyl-ion concentration. The destruction begins when P_H exceeds 6.

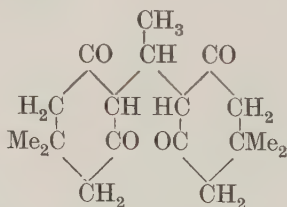
Alcoholic fermentation was last fully dealt with in these Reports two years ago, particularly in regard to the second form of fermentation which produces glycerol according to the equation :



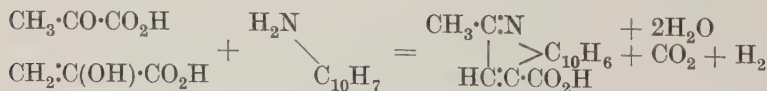
Later, C. Neuberg and J. Hirsch³⁶ distinguished a third form, in which the acetaldehyde is "dismuted" into alcohol and acetic acid, as follows :



The proportions of the products demanded by the above equation have been verified experimentally. In the second form, the acetaldehyde is "trapped" by an alkaline sulphite; the third form occurs in the absence of sulphite, when a feebly alkaline reaction is maintained by potassium carbonate, magnesium oxide, or an alkaline phosphate. Neuberg considers that in all varieties of fermentation pyruvic acid is first formed and is then decarboxylated to acetaldehyde; these two substances occupy a central position in the various schemes. The aldehyde may be trapped by other means than alkaline sulphites. The same object may be attained by dimethylcyclohexanedione³⁷ (dimethyldihydroresorcinol), two molecules of which condense with one of acetaldehyde to form the substance



Lately, M. von Grab³⁸ has been able to fix pyruvic acid itself by means of a biochemical Döbner synthesis of α -methyl- β -naphthacinchonic acid.



³⁶ *Biochem. Z.*, 1919, **100**, 304; *A.*, 1920, i, 798.

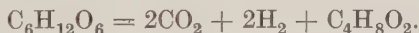
³⁷ C. Neuberg and E. Reinfurth, *ibid.*, 1920, **106**, 281; *A.*, i, 914.

³⁸ Quoted by Neuberg in a useful résumé in *Festschr. d. Kaiser Wilhelm Gesellsch. z. Förderung d. Wissensch. zu ihrem 10-jährigen Jubiläum*, Berlin, 1921, 169.

The central position of acetaldehyde is further revealed by "trapping" it in other fermentations, due to bacteria and moulds. Thus acetaldehyde is an intermediate product in the fermentation of sugar by *B. lactis aerogenes*³⁹ and by *Aspergillus*, *Mucor*, *Monilia*, and *Oidium*.⁴⁰ Moulds decompose pyruvic acid with the formation of acetaldehyde.⁴¹

W. H. Peterson and E. B. Fred⁴² have applied the sulphite fixation method to pentose-fermenting organisms (*B. acetothyllicus* and *Lactobacillus pentoaceticus*). The largest yield was from xylose. The first-named organism also produces acetone, which is perhaps formed from the acetaldehyde by successive condensation, oxidation, and decarboxylation.

Normally, in bacterial fermentations the acetaldehyde is dismutated into alcohol and acetic acid, and the hydrogen, not finding an acceptor, escapes as such; that is, no glycerol is formed. This happens, for instance, in butyric acid fermentation, and Neuberg and Arinstein⁴³ have shown recently that pyruvic acid and acetaldehyde are here also intermediate products. An aldol-condensation product of the former substance is considered to undergo decarboxylation and rearrangement to butyric acid, the nett result being



This Neuberg calls a fourth variety of fermentation.

The number of enzymes known to occur in yeast is considerable. Yet an enzyme of a novel type has been discovered in *carboligase*,⁴⁴ present in maceration juice and so called because it links carbon atoms. The phytochemical reduction of benzaldehyde by yeast results in the formation of benzyl alcohol and, in addition, a hydroxy-ketone of the constitution $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ (or possibly $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_5$), which is considered to be formed from benzaldehyde and acetaldehyde by a benzoin condensation. Apart from its numerous enzymes, yeast is very complex in the manner in which fermentation is accelerated or inhibited by various conditions. O. Meyerhof⁴⁵ observed that when sugar is added to maceration extract there is an induction period, during which no sign of fermentation is observable, but the induction period

³⁹ C. Neuberg, F. F. Nord, and E. Wolff, *Biochem. Z.*, 1920, **112**, 144; *A.*, i, 148.

⁴⁰ C. Cohen, *ibid.*, 139; *A.*, i, 150.

⁴¹ T. Nagayama, *ibid.*, 1921, **116**, 303; *A.*, i, 836.

⁴² *J. Biol. Chem.*, 1920, **44**, 29; *A.*, 1920, i, 911.

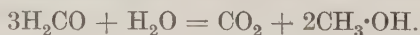
⁴³ Quoted from Neuberg's résumé, *loc. cit.* (reference ³⁸).

⁴⁴ C. Neuberg and J. Hirsch, *Biochem. Z.*, 1921, **115**, 282; *A.*, i, 480.

⁴⁵ *Z. Physiol. Chem.*, 1918, **102**, 185; *A.*, 1919, i, 57.

is abolished by a trace of hexose phosphate. Disodium hydrogen phosphate affects the interval which elapses before maximal fermentation is attained, and other salts, such as sodium chloride, do the same. The induction period is shortened by the addition of aldehydes and of pyruvic acid (Oppenheimer, Neuberg), which function as hydrogen acceptors. The formation of pyruvic acid from dextrose apparently requires the presence of a hydrogen acceptor, which is normally acetaldehyde, derived from the earlier stage of the reaction. The fermentation is therefore autocatalytic. That a hydrogen acceptor is wanting in the induction period was shown by A. Harden and F. R. Henley,⁴⁶ who could shorten the induction period by adding methylene-blue. Lævulose can somewhat hasten the fermentation of dextrose, but acetaldehyde is fifty times as effective. Harden and Henley have also confirmed the salt effect observed by Meyerhof.

As is well known, hexose phosphate has an enormous effect on the course of fermentation. A purely chemical effect which is probably analogous, has been discovered by E. J. Witzemann,⁴⁷ who finds that the oxidation of dextrose to carbon dioxide by hydrogen peroxide is catalysed by disodium hydrogen phosphate; the intermediate formation of a hexose phosphate could not, however, be demonstrated in these experiments. A further purely chemical analogy of another phase of alcoholic fermentation is described by E. Müller;⁴⁸ finely divided osmium decomposes neutral formaldehyde solution according to the equation:



Tissue Oxidation.

The reduction of organic substances by nickel at a high temperature, according to Sabatier and Senderens, is a reversible process, and this induced H. Wieland⁴⁹ to postulate the same reversibility for Paal's process of reduction at the ordinary temperature by palladium. He was able to show that in the complete absence of oxygen, quinol is partly dehydrogenated by palladium black to *p*-benzoquinone; dihydronaphthalene is partly oxidised, partly reduced, to a mixture of naphthalene and tetrahydronaphthalene, after the manner of the Cannizzaro (mutase) reaction. The

⁴⁶ *Biochem. J.*, 1920, **14**, 642; *A.*, 1920, **i**, 914; *ibid.*, 1921, **15**, 175, 312; *A.*, **i**, 480, 642.

⁴⁷ *J. Biol. Chem.*, 1920, **45**, 1; *A.*, **i**, 160.

⁴⁸ *Ber.*, 1921, **54**, [B], 3214.

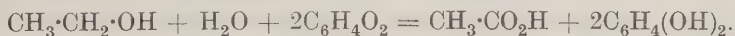
⁴⁹ *Ibid.*, 1912, **45**, 484; 1913, **46**, 3327; 1914, **47**, 2085. Compare also H. G. Denham, *Z. physikal. Chem.*, 1910, **72**, 641; *A.*, 1910, **ii**, 598.

palladium finally contains hydrogen and soon becomes inactive, unless the hydrogen be removed by an "acceptor," which may be methylene-blue, *p*-benzoquinone, or simply oxygen. Later, Wieland interpreted as dehydrogenation also reactions, which are apparently true oxidation (addition of oxygen). He considers the conversion of an aldehyde to an acid as the removal of two hydrogen atoms from the hydrated form of the aldehyde :



Thus formic acid was shown to be an intermediate stage in the oxidation of carbon monoxide to the dioxide.

Starting from this basis, Wieland attempted to explain biological oxidations in the same way. Glucose is partly oxidised by palladium black at the ordinary temperature to carbon dioxide, and the palladium is found to be charged with hydrogen. If *p*-benzoquinone or methylene-blue be added as hydrogen "acceptor," the oxidation proceeds further; 14 per cent. of the glucose was completely burnt to carbon dioxide in one experiment, and with oxygen at 40°, 20 per cent. was completely oxidised. Phenols and other substances which are generally regarded as substrates for an oxydase or peroxydase are likewise oxidised by palladium, which is thereby charged with hydrogen, but tyrosine and uric acid are not affected, so that palladium does not imitate the action of tyrosinase or uricase, which probably are associated with a hydrolytic ferment, absent in the palladium. Ethyl alcohol may be oxidised to acetic acid by means of palladium and *p*-benzoquinone, in the complete absence of free oxygen :



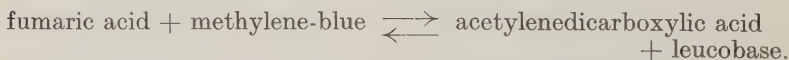
The palladium may be replaced by *Bacterium aceti*, the quinone by methylene-blue, and still oxidation takes place without elementary oxygen intervening. The action of the Schardinger ferment, which reduces methylene-blue in the presence of aldehydes, and the aldehyde mutase of Parnas, which makes aldehydes undergo the Cannizzaro reaction, can all be regarded from the same point of view. The same ferment (dehydrase) in milk can (1) oxidise salicylaldehyde to the acid in the presence of free oxygen, which is then the hydrogen acceptor; (2) in the absence of oxygen act as mutase; half the aldehyde is oxidised, and the other half, acting as acceptor, is reduced to saligenin; (3) in the presence of methylene-blue as acceptor, the aldehyde is only reduced.

Wieland has since apparently abandoned the above line of research, which is now attracting the attention of physiologists,

rather than of organic chemists. In particular, his ideas have been adopted by T. Thunberg in a remarkable paper⁵⁰ on intermediate metabolism. Thunberg has studied the effect of a large number of organic substances on the decoloration of methylene-blue by muscle.

Fresh frog's muscle is cut up very fine and extracted several times with distilled water, in order to remove a substance which by itself reduces methylene-blue. When the muscle has thus been completely inactivated, as little as 0.2 gram is introduced into a "vacuum tube" with 0.02 mg. (about 0.05 millimole) of methylene-blue and a considerable excess (400—800 equivalents) of the substance under investigation. After making the mixture up to 1 c.c., the tube is completely evacuated, filled with water, placed in a thermostat, and inspected at intervals for decoloration. If the substance is a "donator" of hydrogen, the latter is transferred by an enzyme of the muscle ("hydrogen transportase") to the methylene-blue. According to the author, all nutrient material must be able to yield up hydrogen, which is the universal primary fuel of the cell. A substance which does not give up hydrogen cannot be an intermediate metabolite. Hence methylene-blue can be used in order to test substances for their possible significance in intermediate metabolism. There are pronounced differences, even between the members of a homologous series; formic, acetic, butyric, and hexoic acids will give up hydrogen; propionic, isobutyric, and isovaleric acids will not.

Succinic acid is most active and by means of methylene-blue as little as 0.02 mg. of the acid may be detected and estimated.⁵¹ Fumaric acid also gives up hydrogen, but much less readily; the latter reaction is reversible; some methylene-blue remains unreduced, however little be taken, for the acetylenedicarboxylic acid formed enters into competition with the methylene-blue for the hydrogen:



Among hydroxy-acids, glycollic and α -hydroxyisobutyric acids are inactive, but lactic and α - and β -hydroxybutyric acids are oxidised. Their dehydrogenation doubtless results in the formation of an unsaturated hydroxy-acid tautomeric with the keto-acid. As an illustration of the application of the method to metabolic problems, Thunberg suggests that as α - and β -hydroxybutyric acids are about equally ready hydrogen donators, the former acid may also be a product of intermediate metabolism.

⁵⁰ *Skand. Arch. Physiol.*, 1920, **40**, 1; *A.*, 1920, i, 784.

⁵¹ *Svenska Läkareföreningshandlingar*, 1917, **43**, 996; *A.*, 1918, ii, 87.

Among the amino-acids examined, glutamic is the most active, alanine has some effect, but various others are inactive. The removal of hydrogen is considered to lead to an imino-acid, which in turn forms the keto-acid, now fully recognised as the first non-nitrogenous degradation product of amino-acids.

The question naturally arises whether the dehydrogenation of so many diverse substances is effected by one and the same enzyme, or by different ones. Experiments on the destruction by cold, and by heat, led Thunberg to the suggestion that the enzymes are different, the one acting on succinic acid being the most stable. Yet the possibility does not seem excluded, that in Thunberg's destruction experiments only enough of a single enzyme survived to dehydrogenate the most sensitive succinic acid, but not to attack other substances, from which hydrogen is removed less readily.

A most important advance in the investigation of tissue oxidation has been made by F. G. Hopkins,⁵² who has isolated an autoxidisable cell constituent, which has the catalytic properties of a co-enzyme. It is interesting to observe how scientific investigations, at first widely apart, may ultimately converge on the same problem. De Rey-Pailhade⁵³ first showed that extracts of yeast and of many animal tissues reduce sulphur to hydrogen sulphide. They contain therefore, in Thunberg's parlance, a hydrogen donator, which De Rey-Pailhade regarded as a "hydride of protein" and named *phiothion*. Hopkins has now shown this substance to be a dipeptide of cysteine and glutamic acid, and calls it *glutathione*. Its isolation was rendered possible by Mörner's delicate nitroprusside reaction for cysteine, which reaction Heffter, and afterwards V. Arnold,⁵⁴ showed to be given by many tissue extracts. Using this reaction as a guide, Hopkins, by a very complicated process, obtained glutathione, in a yield of 0.01—0.02 per cent. of the fresh tissue employed, from yeast, from muscle, and from mammalian liver. The nitroprusside reaction is also given by proliferating plant tissues, bacteria, and nearly all animal tissues, but not by connective-tissue, nor by blood plasma. The reaction is not given by the fowl's egg, but is given by a thirty-hours' embryo. Glutathione was mostly analysed in the oxidised (disulphide or cystine) form, $C_{16}H_{26}O_{10}N_4S_2$; the thiol form, $C_8H_{14}O_5N_2S$, was obtained crystalline. This dipeptide is quite resistant to proteolytic enzymes, but is hydrolysed by boiling acids to equimolecular proportions of cystine and glutamic acid. The

⁵² *Biochem. J.*, 1921, **15**, 286; *A.*, i, 635.

⁵³ *Compt. rend.*, 1888, **106**, 1683; **107**, 43; *A.*, 1888, 1101.

⁵⁴ *Z. physiol. Chem.*, 1911, **70**, 300; *A.*, 1911, i, 306.

outstanding position of the latter among amino-acids in Thunberg's experiments has already been referred to above.

Hopkins is especially concerned with showing that glutathione exercises real functions in the chemical dynamics of the cell. As in the case of other thiol compounds, the oxidation to the disulphide form depends greatly on the hydrogen-ion concentration. In neutral or slightly alkaline solution, it is oxidised spontaneously by air, but in acid solution it is a less ready donator of hydrogen and is more stable. The oxidised form, on the other hand, is a hydrogen acceptor; fresh tissues placed in a solution of the oxidised form reduce it, as shown by the development of the nitroprusside reaction. Fresh tissues also reduce methylene-blue (as was pointed out above in discussing Thunberg's work), but when they have been kept sufficiently long for their reduction potential to have fallen, so that methylene-blue is no longer reduced, they now oxidise the reduced dipeptide under anaerobic conditions, so that some other substance must act as hydrogen acceptor. The converse reaction, reduction of the disulphide form, depends greatly on the hydrogen-ion concentration. In slightly acid solutions ($P_H < \text{or} = 6.8$), the disulphide form simply competes with methylene-blue for the reducing action of fresh tissues, and as a result, the normal rate of decoloration of the methylene-blue is slowed. In slightly alkaline solution ($P_H > \text{or} = 7.4$), the rate of decoloration is greatly accelerated by the addition of oxidised peptide, which now functions catalytically like a co-enzyme. Herein it differs from succinic acid and the other substances investigated by Thunberg, which are dehydrogenated irreversibly. The reversibility of the action of glutathione is closely connected with its thiol grouping. The autoxidation of this group in cysteine and other compounds has been studied by A. P. Mathews and S. Walker⁵⁵ and by T. Thunberg;⁵⁶ it is much influenced by catalysts.

During the year two reviews on physiological oxidation have appeared; the one, by Dakin, is referred to in the introduction; the other is by P. Woringer and occupies the September number of the *Bulletin de la Société de chimie biologique* (1921, 3, 311—450).

The Chemistry of Muscular Contraction.

We are still very ignorant of the way in which the muscle transforms chemical into mechanical energy. The source of the former is some carbohydrate, glycogen, or its fission product

⁵⁵ *J. Biol. Chem.*, 1909, 6, 289; *A.*, 1909, i, 698.

⁵⁶ *Skand. Arch. Physiol.*, 1913, 30, 285; *A.*, 1914, i, 386.

dextrose, and the presence in muscle of lactic acid (isomeric with a triose) suggested that it had something to do with the energy transformation. Nevertheless, lactic acid accumulates in the living muscle only after violent exertion, and then only to a slight extent, so that there must be a mechanism for its rapid removal. Some interesting light on the origin of lactic acid from carbohydrates has been obtained by G. Embden and his pupils, who found⁵⁷ that muscle press juice contains a substance capable of generating lactic acid, which they called *lactacidogen*. Later,⁵⁸ they described the preparation, in a yield of 0.05 per cent. of the muscle employed, of an osazone identical with that previously obtained by A. von Lebedeff⁵⁹ and W. J. Young⁶⁰ from yeast and recognised as derived from hexose phosphoric acid.

Whether lactacidogen itself is quite identical with the co-enzyme of alcoholic fermentation is not decided, but at any rate the two substances are closely related, and there are some points of similarity between the methods of degradation of the glucose molecule in muscle and in yeast. This similarity has also been insisted on by O. Meyerhof,⁶¹ who found that extracts of muscle contain the co-enzyme of alcoholic fermentation and that this substance plays a part in the respiration and energy transformation in the muscle. Embden and his co-workers have more recently examined the effect of a large number of physiological factors on the lactacidogen content of muscle; a whole number of the *Zeitschrift für physiologische Chemie*⁶² was exclusively devoted to these researches. Some of the main conclusions are as follows. Where muscular activity is greatest, there is most lactacidogen. Frogs contain more at 30° than at 0°, and the increase in lactacidogen is accompanied by a decrease of residual phosphorus. The synthesis of lactacidogen is not under nervous control. The white muscles of rabbits contain about twice as much as the more sluggish red ones, which latter, on the other hand, are richer in non-lactacidogen phosphorus, which is regarded as in reserve. Muscular work and strychnine convulsions decrease the lactacidogen in the white muscles of the rabbit, but not in the red, where, owing to slower action, time is given for its re-synthesis. Since both carbohydrate and phosphoric acid are necessary for the production of lactacidogen, the idea suggested itself of adminis-

⁵⁷ *Biochem. Z.*, 1912, **45**, 45, 63; *A.*, 1912, ii, 1071, 1072.

⁵⁸ *Z. physiol. Chem.*, 1914, **93**, 1; 1917, **100**, 181; 1921, **113**, 1; *A.*, 1915, i, 344; 1917, i, 674; 1921, i, 528.

⁵⁹ *Biochem. Z.*, 1909, **20**, 114; *A.*, 1909, i, 863.

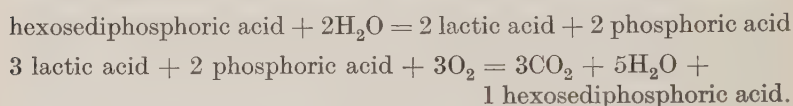
⁶⁰ *Ibid.*, 1911, **32**, 177; *A.*, 1911, i, 422.

⁶¹ *Z. physiol. Chem.*, 1918, **101**, 165; **102**, 1; *A.*, 1918, i, 242, 464.

⁶² 1921, **113**, 1—312; *A.*, i, 528—530.

tering phosphate in order to increase the capacity for work. Numerous experiments on soldiers (with an ergostat and by marching) and on miners are recorded ⁶³ in which 7.5 grams of sodium dihydrogen phosphate per day by the mouth is said to have increased the capacity for muscular work.

O. Meyerhof ⁶⁴ has stated the view that the transformation of hexose to lactic acid is reversible, according to the following scheme :



W. Hartree and A. V. Hill ⁶⁵ have studied the same problem by a purely physical method, measurement of the rate of heat production in a stimulated frog's muscle at different temperatures. The temperature coefficient is 2.8 for 10° and previously the rate of relaxation was shown to have a coefficient of 2.2, so that both processes are purely chemical (the energy liberated by the change from dextrose to lactic acid is only about 16 per cent. of the heat given out, but the 84 per cent. is derived from potential energy due to the effect of lactic acid on some "active" structure or surface). The observations suggest to the authors the mechanical analogy of a large reservoir of compressed air, connected by a narrow tube with an elastic bag with a release valve. When the valve is opened, the air rushes out, at first rapidly and then more slowly until the rate of outflow reaches a value determined by the bore of the connecting tube. Chemically, the large reservoir of energy is the store of glycogen in the muscle, the narrow tube is a catalyst, transforming the glycogen into lactic acid. (The administration of phosphate in Embden's experiments, described above, would be an attempt to widen the tube.) The elastic bag is represented by the balanced action, carbohydrate $\rightleftharpoons$ lactic acid. The opening of the bag is represented by a temporary permeability to lactic acid, produced by the stimulus in some membrane. The lactic acid escapes and causes a change in colloidal properties, resulting in contraction of the muscle-fibres. In the later stages of prolonged stimulation the lactic acid is removed at the same rate at which it is supplied, and a dynamic equilibrium is established, corresponding with the steady production of heat (which has the temperature coefficient of 2.8 per 10°).

⁶³ G. Embden, E. Grafe, and E. Schmitz, *Z. physiol. Chem.*, 1921, **113**, 67; *A.*, i, 529.

⁶⁴ *Pflüger's Archiv*, 1920, **182**, 232, 284; *A.*, i, 76.

⁶⁵ *J. Physiol.*, 1921, **55**, 133; *A.*, i, 527.

Accessory Food Substances and Calcium Metabolism.

A method of estimating the vitamin-*B* content of a solution by its effect on the growth of yeast, as suggested by Williams and others,⁶⁶ has been further criticised by various authors, who find that yeast can synthesise this vitamin. V. E. Nelson, E. I. Fulmer, and R. Cessna⁶⁷ subcultured a yeast on alternate days throughout a year by adding 1 c.c. of the culture to 50 c.c. of a solution containing only salts and sucrose. The maximum concentration of the original constituents was thus 1×50^{-180} . Yet at the end of the year the yeast contained enough vitamin-*B* for the normal growth of rats. Similar conclusions were drawn by M. R. MacDonald and E. V. McCollum⁶⁸ and by A. Harden and S. S. Zilva;⁶⁹ the latter authors showed the presence of vitamin-*B* by its curative effect on polyneuritis in pigeons.

Since we are as yet completely ignorant of the chemical nature of vitamins, the observation by S. S. Zilva and M. Miura⁷⁰ is of some interest, that both the antineuritic and the antiscorbutic vitamins diffuse through a collodion membrane of such permeability as permits the passage of methylene-blue, neutral-red, safranin, and other semi-colloids. The fact that vitamin-*A* is destroyed by atmospheric oxygen,⁷¹ particularly at high temperatures, has been further confirmed,⁷² and exposure to ozone has been found to have the same effect.⁷³

During the year the main interest in vitamins has, however, shifted to the anti-rachitic substance and its connexion with calcium metabolism, which is leading to some new points of view. E. Mellanby⁷⁴ has published in detail his extensive researches on the production of experimental rickets in dogs. He has dieted nearly four hundred puppies and draws the conclusion that among the conditions which induce rickets the most important are a deficiency, in the diet, of calcium and phosphorus and of fat containing the anti-rachitic vitamin. Since the effect of fats in promoting growth runs parallel to their effect in preventing rickets, it is highly probable that the anti-rachitic vitamin is identical with vitamin-*A*. Thus butter fat, through which oxygen is bubbled

⁶⁶ *Ann. Reports*, 1920, **17**, 167.

⁶⁷ *J. Biol. Chem.*, 1921, **46**, 77; *A.*, i, 386.

⁶⁸ *Ibid.*, 1920, **45**, 307; *A.*, i, 480. ⁶⁹ *Biochem. J.*, 1921, **15**, 438; *A.*, i, 702.

⁷⁰ *Ibid.*, 422; *A.*, i, 702. ⁷¹ *Ann. Reports*, 1920, **17**, 165.

⁷² F. G. Hopkins, *Biochem. J.*, 1920, **14**, 725. J. C. Drummond and K. H. Coward, *ibid.*, 734; *A.*, i, 475.

⁷³ S. S. Zilva, *ibid.*, 740; *A.*, i, 475.

⁷⁴ "Special Report Series of the Medical Research Council," No. 61; H.M. Stationery Office, 1921.

for some hours at 120° , loses both its growth-promoting and its anti-rachitic power. Cod-liver oil is particularly active in both directions. Recently a number of papers have appeared on rickets in rats, which have been found suitable for this as well as for many other experiments on vitamins. A. F. Hess, G. F. McCann, and A. M. Pappenheimer⁷⁵ disagreed with Mellanby's view that a deficiency of fat-soluble vitamin is a cause of rickets, but McCollum and his co-workers have confirmed the effect of cod-liver oil in stimulating calcification processes after the production of rickets by defective diets. E. V. McCollum, N. Simmonds, P. G. Shipley, and E. A. Park⁷⁶ give a more complicated explanation of the causation of rickets. According to them, rickets (in rats) is not simply due to a deficiency of vitamin-A, as suggested (for dogs) by Mellanby. To produce rickets, the calcium : phosphorus ratio of the diet must be upset as well, making its calcium content relatively high, its phosphorus content low. With a calcium : phosphorus ratio differing from the optimal for normal ossification, rickets may still be avoided by giving an anti-rachitic substance. The ratio of calcium : phosphorus is considered by these authors to be of "infinitely greater importance" in ensuring normal ossification than the absolute amounts of these elements in the diet. The importance of calcium, as well as of vitamin-A, may perhaps to some extent reconcile the contradictory results of Mellanby and of Hess and his associates. Rather similar views were stated quite recently by V. Korenchevsky,⁷⁷ who concludes that a deficiency of calcium alone may affect the skeleton of rats in a manner suggestive of rickets, and that a deficiency of vitamin-A alone may also produce slight rickets; the changes typical of rickets are, however, most readily produced when the diet is deficient in both calcium and vitamin.

Thus a curious and novel relationship between vitamin-A and calcium metabolism is indicated. The latter is evidently of a complicated nature. P. Rona and D. Takahashi⁷⁸ showed ten years ago, by the method of compensatory dialysis, that 30—40 per cent. of the calcium in serum is non-diffusible, and last year A. R. Cushny⁷⁹ found that when serum is filtered through collodion all the crystalloids pass through, with the exception of some calcium and probably some magnesium. During rickets, there is a slight diminution in the calcium content of serum, during tetany after removal of the parathyroids there is a larger fall, but in either case this is at the expense of the diffusible portion; the

⁷⁵ *J. Biol. Chem.*, 1921, **47**, 395; *A.*, i, 757.

⁷⁶ *Ibid.*, 507; *A.*, i, 757.

⁷⁷ *Brit. Med. J.*, 1921, ii, 547.

⁷⁸ *Biochem. Z.*, 1911, **31**, 336; *A.*, 1911, ii, 302.

⁷⁹ *Ann. Reports*, 1920, **17**, 161.

non-diffusible calcium remains constant, according to L. von Meysenbug and G. F. McCann.⁸⁰ The calcium (and phosphorus) metabolism may also be disturbed, according to S. V. Telfer,⁸¹ by the complete exclusion of bile from the gut, which brings in its train non-absorption of fatty acids and their excretion as calcium soaps in the fæces. The phosphoric acid, normally excreted as calcium salt by the intestine, is now eliminated in the urine.

Apart from metabolic questions, the mechanism of the deposition of calcium in the bones probably has a bearing on rickets. E. Freudenberg and P. György⁸² have attempted to supply a (physico-chemical?) basis for calcification. They conclude that cartilage takes up calcium from a 0.01N-solution until an equilibrium is reached. Tryptic digestion and autolysis, as well as urea and ammonium chloride, inhibit calcium fixation. The authors suggest that normally the organism satisfies the conditions necessary for calcification, except where the process is inhibited by metabolites.

Chemotherapy.

Towards the end of 1920 an advance in chemotherapy became known, which promises to provide a cure for sleeping sickness and to rival the discovery of salvarsan, at least in scientific interest. L. Haendel and K. W. Joetten⁸³ report on a new trypanocide of great activity, which is referred to as "205 Bayer." In a footnote the editor of the journal states that he has exceptionally departed from the principle that no account could be taken of secret remedies, for the composition of the substance is not published, "in consequence of the judicially uncertain and unprotected position of German industry with respect to the former enemy countries." (An allusion to their treatment of German patents.) The authors, working in the Reichs-gesundheitsamt at Berlin, investigated a substance prepared by the Farbenfabriken vorm. Friedr. Bayer & Co., which frees mice, apparently permanently, from Nagana and other pathogenic trypanosomes in doses of 1/20 mg., and is lethal to the host only in doses of about 2 mg., or 40 times as much. The substance is rather specific, for spirochætes and the non-pathogenic *Trypanosoma Lewisii* are not much affected. M. Mayer and H. Zeiss⁸⁴ have published a more extensive investigation of the same substance, and place the subcutaneous

⁸⁰ *J. Biol. Chem.*, 1921, **47**, 541; *A.*, i, 754.

⁸¹ *Biochem. J.*, 1921, **15**, 347; *A.*, i, 700.

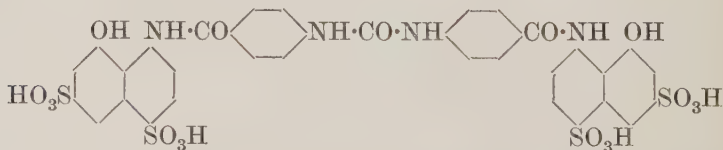
⁸² *Biochem. Z.*, 1921, **121**, 142.

⁸³ *Berl. Klin. Wochenschr.*, 1920, **57**, ii, 821; *A.*, i, 908.

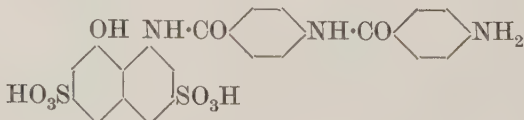
⁸⁴ *Arch. Schiffs u. Tropenhygiene*, 1920, **24**, 257; *A.*, i, 908.

curative dose for mice at 0.06 mg. for *T. brucei* (Nagana), *T. equinum*, *T. equiperdum* (dourine), *T. gambiense* (human sleeping sickness), and *T. rhodesiense*, and the lethal dose at 10 mg., giving the extremely favourable ratio of 1:160. The substance does not kill the trypanosomes very rapidly, like potassium antimonyl tartrate, but takes about forty-eight hours to sterilise the host, apparently by stopping the reproduction of the parasite, of which undivided twin specimens are found in large numbers in the blood. Rats, guinea-pigs, and rabbits can also be cured permanently, and very favourable results have been obtained in natural dourine of horses. C. M. Wenyon⁸⁵ has quite recently confirmed these results for mice and *T. equiperdum* by intravenous injection. In view of the high ratio of lethal dose:curative dose, he observes that for sodium antimonyl tartrate in mice it is only 4. (For man it is <1, so that no cure with antimony can be effected.)

Although the exact composition of "205 Bayer" remains a secret, the curiosity of chemists may perhaps to some extent be satisfied by a perusal of the patents of the years 1914—1916. Farbenfabriken vorm. Friedr. Bayer & Co.⁸⁶ describe the preparation of carbamides of the naphthalene series which are stated to be strongly trypanocidal. By the action of *p*-nitrobenzoyl chloride on 8-amino- α -naphthol-3:5- and -3:6-disulphonic acids (*K* and *H* acids), a compound results which, after reduction of its nitro-group, is condensed with carbonyl chloride to a complex carbamide, for instance,



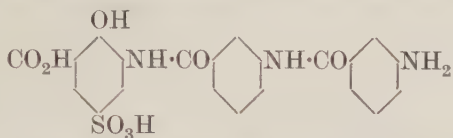
Instead of condensing with carbonyl chloride, the first condensation product may be united with a second molecule of *p*-nitrobenzoyl chloride and reduced, furnishing, for instance, for the 3:6-disulphonic acid the substance



⁸⁵ *Brit. Med. J.*, 1921, ii, 746; *A.*, i, 908.

⁸⁶ D.R.-P. 278122; *Chem. Zentr.*, 1914, ii, 964; *Brit. Pat.* 9472 of 1914; *A.*, 1915, i, 14. See also D.R.-P.P. 289163, 289270—289272; *A.*, 1916, i, 390; *Brit. Pat.* 8591 of 1916; *A.*, 1918, i, 113; and further D.R.-P.P. 284938, 288272, 288273, 289107, and 291351.

and this may, in its turn, be converted into a carbamide sulphonic acid, which is used as the neutral sodium salt. Later patents indicate numerous substances with different substituents in the naphthalene and benzene rings, and the last one mentions a *m*-aminobenzoyl derivative of *m*-aminobenzoylamino-sulphosalicylic acid, without any naphthalene ring. It will be seen that all these



compounds, like polypeptides, contain several times the grouping $\text{NH}\cdot\text{CO}$. They are dyes and resemble Trypanrot in being derivatives of naphthylaminesulphonic acids.

“Bayer 205” is very active on trypanosomes, but much less so on spirochaetes; the reverse is the case with sodium bismuth tartrate, a new therapeutic agent recently introduced in France by R. Sazerac and C. Levaditi.⁸⁷ This analogue of tartar emetic is injected, suspended in oil, and has given very promising results in the treatment of human syphilis, but is not very effective against the Nagana trypanosome. Sodium antimonyl tartrate has of late years been found to be a specific against Kala-azar, due to a protozoon, and against the worm *Filaria sanguinis hominis*, but the administration of antimony in sleeping sickness has not been quite successful. There is at present some falling off in attempts to synthesise arsenic compounds which might rival salvarsan or its immediate derivatives, but our knowledge concerning the latter substance and its technical impurities is increasing. The biological testing of salvarsan has revealed the considerable variation in the toxicity of commercial samples and one of the reasons for this variation seems to be the use of sodium hyposulphite as a reducing agent. R. G. Fargher and F. L. Pyman⁸⁸ found that the slight sulphur content of technical preparations is due to admixture with a substance containing sulphur which enters the molecule in the reduction of 3-nitro-4-hydroxyphenylarsinic acid by sodium hyposulphite; with hypophosphorous acid this introduction may be avoided. W. G. Christiansen⁸⁹ has confirmed these results and states that the product prepared by hypophosphorous acid is relatively non-toxic. H. King⁹⁰ has now identified sulphur compounds which were regularly formed under the conditions employed by him in the reduction, to the

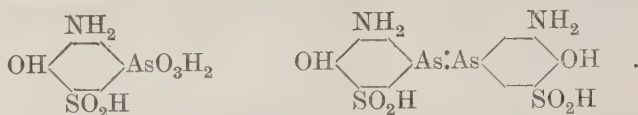
⁸⁷ *Compt. rend.*, 1921, **172**, 1391; **173**, 338; L. Fournier and L. Guénot, *ibid.*, 1921, **173**, 674; *A.*, i, 908.

⁸⁸ *T.*, 1920, **117**, 373.

⁸⁹ *J. Amer. Chem. Soc.*, 1920, **42**, 2402.

⁹⁰ *T.*, 1921, **119**, 1107.

extent of about 10 per cent.; this amount is large enough to account for all the sulphur of most specimens. These compounds are 3-amino-4-hydroxy-5-sulphinophenylarsinic acid, and (to a smaller extent) the corresponding arseno-derivative,



The latter is found to be twice as toxic to mice as salvarsan prepared by hypophosphorous acid.

Artificial Sweetening Agents.

Apart from saccharin, the only artificial sweetening agent which has met with practical application is dulcin, $\text{EtO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$. In the case of both substances, even the slightest modifications in the molecule generally abolish the sweet taste entirely. Thoms and Nettesheim⁹¹ find that the methoxy-compound corresponding with dulcin is somewhat sweet, and the hydroxy-compound only very slightly so; all other derivatives had no sweet taste at all.

Pure saccharin, the more powerful of the two, is generally stated to be 550 times as sweet as sucrose, but Th. Paul⁹² has shown that the comparison of sweetening powers is no simple matter. Saccharin and dulcin mutually reinforce one another; this pharmacological effect has been alleged to occur with a number of drugs and is well established in the case of opium alkaloids, for instance. As an example, Paul mentions that when 280 mg. of saccharin and 120 mg. of dulcin are dissolved in 1 litre of water, they cause the same sweetness as 535 mg. of saccharin by itself. A further complication⁹³ is that at various concentrations of the solution the ratio of the sweetening power of saccharin to sucrose is not constant and may vary from 200 in concentrated solution to 700 in dilute solution. Similarly, the ratio for dulcin varies from 70 to 350. In other words, both these substances are relatively sweeter in dilute solution. This phenomenon is not shown by the various sugars, which have a constant ratio of sweetness, independent of the concentration. The physiological effect of these synthetic substances is apparently of a different nature from that of the sugars.

A third artificial sweetening agent has lately become the subject of a patent⁹⁴ in which it is claimed that it is two thousand times as

⁹¹ *Ber. deutsch. Pharm. Ges.*, 1920, **227**, 295.

⁹² *Chem. Ztg.*, 1921, **45**, 38; *A.*, i, 109.

⁹³ *Ibid.*, 705.

⁹⁴ S. Furukawa, *Jap. Pat.* 35332; *A.*, 1920, i, 676.

sweet as sucrose, so that it would be the sweetest substance known. This is the α -*anti*-aldoxime of perillaldehyde; it has been further described by S. Furukawa and Z. Tomizawa.⁹⁵ Perillaldehyde, $C_9H_{13}\cdot CHO$, is a levorotatory liquid, b. p. $104^{\circ}/9$ mm., of unknown constitution, which forms 44—57 per cent. of the essential oil of the leaves of *Perilla nankinensis* Dene., a Labiate known in Japan as "Shiso." The leaves are used as a vegetable or condiment. The oil of *P. ocymoides*, L., is a technical product in Eastern Asia (Wehmer, "Die Pflanzenstoffe," p. 822). According to Furukawa and Tomizawa, the *anti*-aldoxime of perillaldehyde, two thousand times as sweet as sucrose and four to eight times as sweet as saccharin, differs in this respect entirely from the β -*syn*-aldoxime, which is not sweet at all. These two substances therefore provide a novel and interesting example of the different physiological behaviour of stereoisomerides which has so far been principally studied in enantiomorphs (adrenaline, hyoscyamine, hyoscine). Perillonitrile, $C_9H_{13}\cdot CN$, is half as sweet as saccharin. It is a curious fact that the *anti*-oxime of perillaldehyde was described as long ago as 1910,⁹⁶ but that its sweet taste, now the reason for a patent, was not then noticed. Possibly organic chemists should more frequently taste their new compounds than they do at present.

GEORGE BARGER.

⁹⁵ *J. Chem. Ind. Tokyo*, 1920, **23**, 342; *A.*, 1920, i, 751.

⁹⁶ Schimmel & Co., *Bericht*, October, 1910; *A.*, 1910, i, 759.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

THE investigations in the past year have in the main followed the lines of previous years : there are, however, signs of more movement. In France, the *Annales de la Science Agronomique* has been restarted, under the able editorship of M. Albert Bruno, and already there is an increase in the output of scientific work. In England and in America, investigations begun after the Armistice are reaching the stage of publication, and certain directions of specialisation can now be observed. These will be indicated under the various headings.

Soil Investigations.

British soil investigators are studying the biological factors; American workers are ascertaining the properties and relationships of the soil solution and of the soil acidity; whilst Continental workers are studying the physico-chemical relationships of the soil. This course is economical of time and effort, but it would be attended by grave disadvantages if the specialisation proceeded so far as to obscure the fact that all three aspects of the subject are of vital importance to the study of soil fertility.

The Soil Solution.

The soil retains by absorption and surface attractions some 10 to 20 per cent. of its weight of water, distributed as films over its particles. The water dissolves some of the soil constituents, forming a solution which is of obvious importance as the medium through which plants and micro-organisms derive their food; indeed it may be regarded as the culture solution for the plant. Experimental work, however, is hampered by the difficulty of separating it from the soil; when soil contains moisture in percentages suitable for plant growth, the solution is held by the soil particles with such force that no ordinary means will remove it.

Various methods have been suggested for isolating the solution from the soil. Reasons are advanced for supposing¹ that the

¹ F. W. Parker, *Soil Sci.*, 1921, **12**, 209; *A.*, i, 914.

solution obtained by Ischerekov's displacement method² gives a more faithful representation of the soil solution than the other methods which have been used; ethyl alcohol was the best of the displacing fluids tested, and was without observed influence on the composition of the soil solution; successive portions of the displaced solution gave the same freezing-point depression and contained the same amount of total solids, whilst the concentration was inversely proportional to the moisture of the soil.

It is, however, difficult to extract the solution, and methods have been devised for studying it in situ. It is suggested³ that a study of the vapour pressure of the soil would give much valuable information, whilst the depression of the freezing point has been much studied by Bouyoucos in America. Hoagland and his colleagues⁴ show that the latter method leads to substantially the same conclusions as the 1 : 5-water extraction method used in the United States.⁵

The water extract has not quite the same composition as the soil solution, but is not greatly dissimilar. When concentrated to have the same freezing point, it presumably resembles the actual solution also in concentration and should then undergo no change when placed in contact with soil. Experiment showed that this was the case, and probably for the first time in history a solution was poured through the soil and came out unchanged in composition.

The relationship between the concentration of the soil solution and plant growth has previously been studied in the case of barley;⁶ similar results have now been obtained with maize, horse beans, potatoes, and turnips.⁷ The concentration at any point in the soil is not significantly reduced until the plant root actually reaches it, that is, there is no drift of solutes in the soil apart from the movement due to drainage.

Apparently, however, the fact that a substance occurs in the soil extract affords no certain proof that it can be absorbed by plants. Orthoclase yields up potassium to water, but the dissolved potassium was not absorbable by wheat. It became available, however, when the solutions were treated with a mixture of hydrochloric and nitric acids.⁸ Apparently the solute complex is not dissociated, and the plant is unable to take up the undissociated material.

² *Zhur. Opuin. Agron.*, 1907, **8**, 147.

³ M. D. Thomas, *Soil Sci.*, 1921, **11**, 409.

⁴ D. R. Hoagland, J. C. Martin, and G. R. Stewart, *J. Agric. Res.*, 1920, **20**, 381; *A.*, i, 214.

⁵ G. R. Stewart, *ibid.*, 1918, **12**, 311.

⁶ *Ann. Reports*, 1918, **15**, 173; 1919, **16**, 172.

⁷ G. R. Stewart and J. C. Martin, *J. Agric. Res.*, 1921, **20**, 663.

⁸ J. F. Breazeale and L. J. Briggs, *ibid.*, 615; *A.*, i, 388.

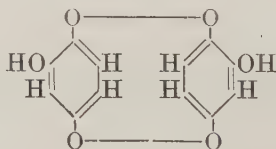
The variation in composition of soil solution brought about by plant growth affects the degree of dispersion of the colloidal material of the soil; a large increase in dispersion was observed when the soil solution was depleted as the result of absorption of solutes by the plant.⁹

The same change has been studied in a different manner in Germany, where Wiegner's method has been successfully used by von Seelhorst to study the changes in physical condition of soil brought about by cropping and manuring.¹⁰

There is a constant interchange between the colloids of the soil and the soil solution, and the ions affect the state of coagulation of the colloids.¹¹

Soil Constituents.

The soil constituents fall into two great groups—organic substances which have been synthesised in the growing plant and then returned to the soil either directly or through the bodies of animals or micro-organisms, and inorganic substances derived from the minerals in the soil, which very often have also passed into plants and been liberated on the decay of the leaves, stems, or roots. Among the organic constituents, one of the most interesting is humus, a black, sticky substance to which important properties have been attributed, although it must be admitted that the direct evidence is not very strong. Two views have been put forward as to its origin. Beckley¹² supposes that the carbohydrates decompose to form hydroxymethylfurfuraldehyde, which then condenses to form humus; some experimental evidence is given for this view, which has also been put forward independently.¹³ Eller and Koch,¹⁴ on the other hand, suppose that humus is formed by oxidation of quinones which arise by the elimination of water from hexoses. They assign to it the formula $C_6H_4O_3$:



⁹ D. R. Hoagland and J. C. Martin, *J. Agric. Res.*, 1920, **20**, 397; *A.*, i, 215.

¹⁰ C. von Seelhorst, W. Geilmann, and H. Hubenthal, *J. Landw.*, 1921, **69**, 5; W. Geilmann and A. von Hauten, *ibid.*, 105.

¹¹ L. Casale, *Staz. sperim. agrar. ital.*, 1921, **54**, 65.

¹² V. A. Beckley, *J. Agric. Sci.*, 1921, **11**, 69; *A.*, i, 227.

¹³ J. Marcusson, *Ber.*, 1921, **54**, [B], 542; *A.*, i, 313.

¹⁴ *Ibid.*, 1920, **53**, [B], 1469; *A.*, 1920, i, 733. See also W. Eller, *Brennstoff-Chem.*, 1921, **2**, 129; *A.*, i, 506; H. Stoltzenberg and M. Stoltzenberg-Bergius, *Z. physiol. Chem.*, 1920, **111**, 1; *A.*, i, 32.

Against this view it is urged¹⁵ that natural humus, unlike benzene derivatives, cannot be sulphonated or nitrated, whilst other experiments indicate that the acidity is due to carboxyl and not to phenolic groups.¹⁶

Several interesting papers have appeared on clay, using the word in the sense of the soil investigator, and not of the ceramic chemist. This is the fraction of soil the particles of which are 0.002 mm. or less in diameter. This has been subdivided into twenty-six fractions by elutriation methods and each fraction fully analysed. About 80 per cent. of the total clay had a fairly constant composition, closely approximating to the theoretical clay complex, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The remaining fractions, consisting of the coarser grades, showed a gradually increasing silica content.¹⁷

A suggestive investigation which recalls some earlier work by Schloesing père has been published from the United States Bureau of Soils.¹⁸ Aqueous extracts of soil frequently contain a considerable amount of colloidal material, which renders them opalescent even after standing, and no ordinary filtration suffices to clear them. Quantities of this material have been extracted from soil and examined; it consists mainly of hydrated silicate of aluminium with varying amounts of ferric hydroxide, silicic acid, organic matter, and possibly aluminium hydroxide, with small amounts of calcium, magnesium, potassium, and sodium. It showed marked colloidal properties and to it is attributed much of the colloidal characteristics of the soil. Its power of absorbing gaseous ammonia and dyestuffs was investigated, and on this is based a method for estimating the amount present in soils; in the case examined, this was 28 per cent., the clay on the American basis (0.005 mm. diameter) being 35.9 per cent. The material is called "ultra-clay"; it may be substantially the same as "clay" in the British sense (0.002 mm. diameter).

Soil Acidity.

Many soils are greatly improved by the addition of lime, and the obvious explanation is commonly put forward that they have in some way become acid and therefore infertile, but that fertility is restored on neutralisation. The explanation was seriously called in question when it was shown that absorption would account for many of the observed facts, and the tendency in recent years has been to analyse the phenomena more closely.¹⁹

¹⁵ J. Marcusson, *loc. cit.*; *Z. angew. Chem.*, 1921, **34**, 437; *A.*, ii, 590.

¹⁶ Sven Odén, *Koll. Chem. Beihefte*, 1919, **11**, 75; *A.*, i, 393.

¹⁷ E. Blanck and F. Preiss, *J. Landw.*, 1921, **49**, 73.

¹⁸ C. J. Moore, W. H. Fry, and H. E. Middleton, *J. Ind. Eng. Chem.*, 1921, **13**, 527.

¹⁹ For critical discussion, see E. A. Fisher, *J. Agric. Sci.*, 1921, **11**, 19; *A.*, i, 215; A. Demolon, *Ann. Sci. Agron.*, 1920, **37**, 97.

An acid filtrate is obtained when a solution of a neutral salt is poured through the soil. In the case of potassium nitrate and sodium chloride, this has been traced to aluminium and iron rendered soluble by basic exchange; whilst in the case of calcium acetate and potassium acetate it is due to acetic acid liberated either by replacement of the hydrogen of hydrous silicates or by selective absorption of the basic element in the salt solution.²⁰

Other causes of acidity have been investigated. It is not clear, however, that the true acidity as measured by hydrogen-ion concentration is ever sufficient in nature greatly to affect the growth of plants. It is easy to be misled by the results of laboratory experiments. Degrees of acidity which proved inhibitive to micro-organisms such as *Azotobacter* and *Actinomycetes* had no observable effect on the growth of wheat in culture solutions.²¹ Moreover, crops grown in sand cultures showed a higher degree of tolerance of acidity than those grown in culture solutions.²² Indeed, sand cultures containing solutions of P_H ²³ value 3 and therefore acid gave better growth than those more nearly neutral. In the latter case, however, the plants were chlorotic, and it is possible that the results are due to lack of available iron. Natural soils present even more complexity, since they show a high degree of buffering, which coarse sand does not.²⁴

Meanwhile, however, results are being accumulated and the question of method is important. The colorimetric method for determination of P_H values is so much more rapid than the electro-metric method that it would be universally adopted if it were equally trustworthy. A careful examination has revealed²⁵ some of its defects and has emphasised the effect of fineness of division of the soil.

Methods of controlling the soil reaction are also being worked out. It is suggested²⁶ that addition of sulphur to soil might produce acidity which would be useful in checking the potato scab organism (*Actinomyces chromogenus*, Gasperini). Good field results are recorded, especially where the organism that oxidises the sulphur is added; the yield of potatoes was increased by 50 per cent., whilst the percentage of unsaleable scabby potatoes fell from 58 to 29 per cent. of the total crop.²⁷

²⁰ R. H. Robinson, *Soil Sci.*, 1921, **11**, 353; *A.*, i, 644. See also J. J. Mirasol, *ibid.*, 1920, **10**, 153; *A.*, i, 88.

²¹ H. F. A. Meier and C. F. Halstead, *ibid.*, 1921, **11**, 325.

²² A. G. McColl and J. R. Haag, *ibid.*, 1921, **12**, 69.

²³ P_H is the expression used for $-\log[H^+]$.

²⁴ R. E. Stephenson, *Soil Sci.*, 1921, **12**, 145.

²⁵ E. A. Fisher, *J. Agric. Sci.*, 1921, **11**, 45.

²⁶ J. G. Lipman, A. L. Prince, and W. A. Blair, *Soil Sci.*, 1921, **12**, 197.

²⁷ W. H. Martin, *ibid.*, 1921, **11**, 75; see also J. G. Lipman, A. W. Blair, W. H. Martin, and C. S. Beckwith, *ibid.*, **11**, 87.

Another direction for utilising the acidity produced by addition of sulphur to soil is in removing the last of the alkalinity from alkali soils after most of the salts have been washed out by irrigation water.²⁸

The converse problem of reducing acidity by addition of lime or of calcium carbonate has been studied. The relationship between added calcium hydroxide and P_{H} value (as measured by electro-metric titration) is not simple,²⁹ and some of the acid soils, for example, in Oregon, do not respond to lime treatment.³⁰ No explanation is forthcoming and further work is called for. Moreover, it appears that soils contain not only calcium but magnesium carbonate also, and these do not behave alike.³¹

In general, however, acidity is rectified by addition of calcium carbonate, and from the practical point of view it is desirable to have some method that will show how much must be added to soil to ensure a neutral reaction. The Hutchinson-McLennan method is shown to give useful indications.³² In addition to calcium carbonate, other materials can be used; experiments are recorded with a slag described as "dicalcium silicate."³³

Soil problems, however, are very complex and lime must not be regarded solely as a neutralising agent. Reference has already been made to the chlorosis induced in sand cultures when neutrality was maintained. Other observations indicate that the chlorosis induced by lime in calcareous soils is due to depression in the availability of iron. Evidence from ash analysis of chlorotic plants seems to point to lack of iron as one cause of the chlorosis, a possible contributory cause being excess of lime (see p. 208). Rice became chlorotic in calcareous soils with ordinary percentages of water, but it made normal healthy growth when the soil was submerged. It is suggested that special roots are formed under submerged conditions better able to assimilate iron than the ordinary root.³⁴

A further effect of lime, which is often harmful, is to influence the potash supply to the plant.³⁵ It appears that potassium assimilation by plants is adversely affected by lime when only small amounts of potassium are present. In practice, this particular difficulty can be overcome by supplying potassic fertilisers.

Further, the phosphate supply is affected by calcium carbonate.

²⁸ P. L. Hibbard, *Soil Sci.*, 1921, **11**, 385; J. L. Lipman, *ibid.*, 1916, **2**, 205.

²⁹ C. O. Swanson, W. L. Latshaw, and E. L. Tague, *J. Agric. Res.*, 1921, **20**, 855.

³⁰ R. H. Robinson and D. E. Bullis, *Soil Sci.*, 1921, **11**, 363; *A.*, i, 644.

³¹ F. Hardy, *J. Agric. Sci.*, 1921, **11**, 1; *A.*, i, 215.

³² Ch. Brioux, *Ann. Sci. Agron.*, 1920, **37**, 233.

³³ C. J. Schollenberger, *Soil Sci.*, 1921, **11**, 261.

³⁴ P. L. Gile and J. O. Carrero, *J. Agric. Res.*, 1920, **20**, 33.

³⁵ P. Ehrenberg, *Landw. Jahrb.*, 1919-20, **54**, 1.

The retention by soil of the P_2O_5 of superphosphate is regarded³⁶ as a chemical interaction if calcium carbonate is present, but as a physical adsorption if it is absent. In the former case dicalcium phosphate is formed so rapidly that the whole of the phosphate is precipitated within a very restricted range: this becomes slowly converted into tricalcium phosphate.

The physical adsorption in non-calcareous soils is rather different and less rapid, so that the phosphate washes further down into the soil. On non-calcareous soils, therefore, phosphatic manuring should be more effective than on calcareous soils.

As always happens in soil investigations, it is necessary to distinguish clearly between the phenomena observed in soils devoid of vegetation and those on which plants are growing. The former present the simpler case and are necessarily studied first; the plant introduces so much complication that even now little has been ascertained with certainty. The relationships between soil reaction and absorption of ions are complicated in presence of the growing plant by the circumstance that different plants vary in their power of absorbing nutrients from the soil: maize could absorb difficultly soluble phosphates from acid soils only; mustard could take it under more nearly neutral conditions.³⁷

These various observations must not, however, be taken as indicating that acid soils are in general more favourable than neutral soils for the yielding up of nutrients to the plant. It is true that excess of calcium carbonate seems to be harmful in some cases, but there is also evidence that plants usually obtain phosphates more easily from neutral than from acid soils.³⁸

Effect of Salts on Soil.

Just as lime has a complex action on soil so also do various salts. There is an exchange of bases³⁹ which may lead to an acid reaction, as already stated. There are also important physical effects arising out of the flocculation of clay by dissolved salts. These have been studied at Rostock in an important investigation by Nolte:⁴⁰ they have also received attention in America. In the American investigations, sodium salts cause clay to become harder and less permeable to water. This is objectionable in regions where irrigation is necessary, and in such cases the water must be examined to see if it

³⁶ W. H. Harrison and S. Das, *Pusa Memoirs Chem. Series*, 1921, **5**, No. 9.

³⁷ M. Wrangell, *Landw. Versuchs. Stat.*, 1920, **96**, 209.

³⁸ G. S. Fraps, *Texas Agric. Expt. Station Bull.*, 1920, 267; also O. M. Shedd, *Soil Sci.*, 1921, **11**, 111.

³⁹ For details, see W. P. Kelley and A. B. Cummins, *ibid.*, 1921, **11**, 139; *A.*, i, 388.

⁴⁰ O. Nolte, *J. Landw.*, 1919, **67**, 267.

contains more sodium and potassium than calcium and magnesium; if so, its continued use is likely to be harmful. The suggestion is made that addition of soluble calcium or aluminium compounds to the water might overcome the difficulty.⁴¹

Soil Analysis.

One of the most difficult problems for the agricultural chemist is that of soil analysis. He is expected to analyse soils and on the basis of his results to give recommendations as to manuring. Unfortunately, the problem is particularly difficult; in most cases insoluble on our present knowledge. The trouble arises from the fact that no two methods give the same results; it is possible from the Rothamsted soils to extract percentages of K_2O varying from 0.001 to 5 per cent., according as one extracts with water or adopts drastic fusion methods. Two important summaries and discussions of the German results⁴² show the relative importance there attached to the various factors, and indicate high-pressure steam as a suitable agent in potash determinations. Another suggestion is that the ratio of soluble to total K_2O or P_2O_5 (using 1 per cent. citric acid as the agent for soluble P_2O_5 and 10 per cent. hydrochloric acid for soluble K_2O) is more useful than either figure taken separately in explaining fertiliser results. The authors carefully disclaim, however, any predictions of fertiliser requirements.⁴³ It is suggested also that the plant is able to extract from a soil more K_2O but less P_2O_5 than is dissolved by 1 per cent. citric acid.

The use of 0.2*N*-nitric acid for soil analysis has been further discussed⁴⁴ and also that of hydrochloric acid.⁴⁵

Mechanical analysis of soil,⁴⁶ at present a very tedious process, promises to be simplified by using sodium carbonate as the deflocculating agent instead of ammonia, whilst the use of the centrifuge still further accelerates the process.⁴⁷

Finally, a promising attack has been made on the exceedingly difficult problem of determining the amount of colloidal material in soils.⁴⁸

⁴¹ C. S. Schofield and F. B. Headley, *J. Agric. Res.*, 1921, **21**, 265.

⁴² J. König and J. Hasenbäumer, *Landw. Jahrb.*, 1920, **55**, 184; J. König, J. Hasenbäumer, O. Kleine-Möllhoff, and M. L. Plouski, *ibid.*, 1921, **56**, 439.

⁴³ O. Lemmermann, L. Fresenius, and H. Wiesmann, *Landw. Versuchs. Stat.*, 1921, **98**, 155.

⁴⁴ O. M. Shedd, *Soil Sci.*, 1921, **11**, 111.

⁴⁵ F. Munter, *Landw. Versuchs. Stat.*, 1919, **94**, 181.

⁴⁶ For a discussion of methods, see U. Pratolongo, *Ricerche R. Scuola Sup d'Agric. di Milano*, 1920, **6**, 97.

⁴⁷ A. F. Joseph and F. J. Martin, *J. Agric. Sci.*, 1921, **11**, 293.

⁴⁸ C. J. Moore, W. H. Fry, and H. E. Middleton, *J. Ind. Eng. Chem.*, 1921, **13**, 527; *A.*, ii, 608.

Environmental Conditions.

A detailed study of soil temperatures⁴⁹ brings out the interesting fact that the top 6 inches of soil is on the whole rather warmer than the air, so that the temperature conditions are more favourable to micro-organisms and plant roots than might be expected.

Water.

Soil water is generally divided into three forms—gravitational (the excess that can drain away), capillary (the free water held to the surface of the soil particles by capillary forces), and hygroscopic (water which is in equilibrium with the vapour of a saturated atmosphere). The division is convenient and intelligible. Bouyoucos, who has for several years studied the freezing of water in soil, substitutes⁵⁰ the following classification, which has the advantage of being more specific :

Gravitational. Unsuitable for plant growth.

Free. Freezing readily near 0° or just below (-1.5°). Readily available for plants.

Unfree	{	Not freezing until -4° or lower. Capillary adsorbed; only very slightly available for plant growth.
		Not freezing at -78° . Combined: either water of hydration or water of solid solution; unavailable for plants.

According to this scheme, the wilting point corresponds closely with the water that fails to freeze at -1.5° , that is, the unfree water. He claims⁵¹ that the amount of "unfree" water in the soil is a constant, not, as Keen supposed, a function of the total water.

He further argues⁵² that the solution around the soil particles and in the very fine capillary spaces is less concentrated than the mass of the soil solution; this is, of course, against the current conventions.

The physical principles involved in the distribution of water in the soil have been discussed by Wilsdon,⁵³ whilst an admirable account has appeared of the relationship of clay to the adsorption of water.⁵⁴

The water supply of the soil affects not only the rate of growth of the plant, but also to some extent its composition. The concen-

⁴⁹ B. A. Keen and E. J. Russell, *J. Agric. Sci.*, 1921, **11**, 211.

⁵⁰ G. Bouyoucos, *Soil Sci.*, 1921, **11**, 33.

⁵¹ *Ibid.*, 255.

⁵² *Ibid.*, 131.

⁵³ B. H. Wilsdon, *Pusa Memoirs, Chemical Series*, 1921, **6**, No. 3.

⁵⁴ Sven Odén, *Trans. Faraday Soc.*, 1921, **17**, 244.

tration of cell sap has been shown to depend on the moisture content of the soil; apparently this is the chief factor concerned. A low concentration (induced by high moisture content) is associated with rapid vegetative growth; a high concentration with slower growth but with fruit bud formation.⁵⁵

Soil Organisms.

The relationships existing between the growing plant and the micro-organic population of the soil are gradually being elucidated,⁵⁶ but the papers published this year deal largely with matters of detail. The range of substances decomposable in the soil by micro-organisms is remarkable, and includes some of the very stable hydrocarbons such as paraffins, benzene, toluene, etc.;⁵⁷ it is even suggested that soil organisms could be used in gas analysis for discriminating between certain hydrocarbons.

Most of the investigations, however, deal with the nitrogen cycle. Many organisms are capable of decomposing protein with formation of ammonia; it is not usual to discriminate between these in soil investigations, but only to count them; a comparison has been made of different counting methods adopted.⁵⁸

In nature, the ammonia is almost invariably oxidised bacterially to nitrate, and attempts have several times been made in France to utilise this action on the manufacturing scale: a new method is suggested in which ammonium salts percolate through peat or volcanic scorix.⁵⁹

The bacterial fixation of nitrogen continually attracts attention: it is effected by two groups of organisms, *Azotobacter* and *Clostridium*. The former is usually regarded as the more important; it assimilates nitrogen more slowly at ordinary laboratory temperature than at 27°, but fixes more per unit of mannite consumed.⁶⁰ The effects of coloured light and of uranium salts have also been studied. A method of estimating the numbers of *Clostridium* in the soil has been devised,⁶¹ and the view is put forward that it is more numerous than *Azotobacter* and probably plays a more important part in the fixation of nitrogen.

⁵⁵ H. S. Reed, *J. Agric. Res.*, 1921, **21**, 81.

⁵⁶ For a recent summary, see E. J. Russell, *Ann. Sci. Agron.*, 1921, **38**, 49.

⁵⁷ J. Tausz and M. Peter, *Centr. Bakt. Par.*, 1919, [ii], **49**, 497; *A.*, 1920, i, 911.

⁵⁸ Z. N. Wyant, *Soil Sci.*, 1921, **11**, 295.

⁵⁹ E. Boullanger, *Ann. Inst. Pasteur*, 1921, **35**, 575; *A.*, i, 836.

⁶⁰ E. Kayser, *Compt. rend.*, 1920, **171**, 969; *A.*, i, 79; *ibid.*, 1921, **172**, 183, 493, 939, 1133; *A.*, i, 208, 479.

⁶¹ G. Truffaut and N. Bezssonoff, *ibid.*, 1921, **172**, 1319.

A third group of organisms acts in symbiosis with leguminous plants and is closely related in activity to the growth of the plant.⁶² Morphologically they present many features of interest.⁶³

Other organisms seem concerned in the loss of nitrogen from soil, some of which is presumably brought about by an evolution of gaseous nitrogen. Although little is known of the mechanism of the process, further measurements have been made of the quantities involved. In the New Jersey cylinder experiments, which extended over a period of twenty years,⁶⁴ the loss has usually been of the order of 100 lb. per acre for the first fifteen years; where, however, green manure was used, there was no loss, but a gain.

Partial Sterilisation.

Further results have been published⁶⁵ showing the increase of crop yield resulting from heat treatment of soil. The effects persisted for several crops; they varied somewhat, however, with the different layers of soil. The introduction of untreated soil did not wholly counteract the effect of steaming, showing that the decomposition of soil materials is a potent factor in determining the effect.

Owing to the cost and limited application of heat, efforts are continued to find some chemical agent capable of modifying the soil population in the desired direction. Studies have been made of *p*-dichlorobenzene, which gave promising results against the Peach-tree Borer (*Sanninoidea exitiosa*, Say), a destructive pest of peach trees,⁶⁶ and of the physical and other conditions affecting the use of carbon disulphide as a soil sterilising agent.⁶⁷

Phenol has also proved effective, but it is liable to certain obscure interactions with soil constituents and to biochemical decomposition in the soil whereby its value is much diminished.⁶⁸

Chloropicrin and formaldehyde are useful partial sterilising agents,⁶⁹ and their effect on germination has been discussed.⁷⁰

⁶² A. L. Whiting and W. R. Schoonover, *Soil Sci.*, 1920, **10**, 441.

⁶³ F. Löhnis and R. Hansen, *J. Agric. Res.*, 1921, **20**, 543.

⁶⁴ J. G. Lipman and A. W. Blair, *Soil Sci.*, 1921, **12**, 1.

⁶⁵ Viscount Elveden, *J. Agric. Sci.*, 1921, **11**, 197.

⁶⁶ A. Peterson, *Soil Sci.*, 1921, **11**, 305.

⁶⁷ B. R. Leach, *ibid.*, 1921, **10**, 421.

⁶⁸ N. N. Sen Gupta, *J. Agric. Sci.*, 1921, **11**, 136.

⁶⁹ E. J. Russell, *J. Roy. Hort. Soc.*, 1920, **45**, 237.

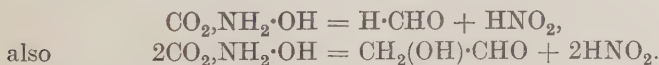
⁷⁰ E. Miège, *Compt. rend.*, 1921, **172**, 170 (chloropicrin); A. H. Hurd, *J. Agric. Res.*, 1920, **20**, 209 (formaldehyde).

The Chemistry of the Living Plant.

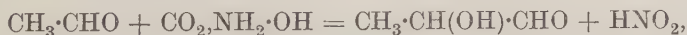
Photosynthesis.

The rapid production of sugar in the leaf from carbon dioxide continues to evoke a great volume of research. Baeyers' original hypothesis still holds the field, and there is no generally recognised alternative to the view that the first product is formaldehyde, which subsequently condenses to sugar. The key-sugar in carbon metabolism, both in the up- and the down-grade processes, appears to be glucose. The pentoses, however, are invariably present and play an important part in plant processes, entering into the composition of the nucleus, of certain cell-walls and of mucilage,⁷¹ and helping considerably in determining succulence.⁷²

Numerous investigations have shown that formaldehyde is obtainable in circumstances more or less comparable with those obtaining in natural photosynthesis. The more notable papers include one from a physico-chemical laboratory where the chemical pitfalls are avoided,⁷³ and one from a physiological laboratory where the plant conditions are fully recognised.⁷⁴ In the latter it is claimed that the production of formaldehyde results from the decomposition of chlorophyll and is not directly dependent on the presence of carbon dioxide. An interesting discussion, which, moreover, invites controversy, is contained in the Hugo Müller lecture.⁷⁵ An alternative view is put forward by Mazé in which the principal part is assigned to hydroxylamine. This base is supposed to arise in the leaves by reduction of nitric acid (nitrates being the recognised nitrogenous nutrients of plants and absorbed in considerable quantities from the soil); it combines with carbon dioxide and changes as follows :



These products are actually found in the leaves of the elder. The glycollaldehyde may become reduced to acetaldehyde; this reacts to produce lactaldehyde and nitrous acid,



⁷¹ F. F. Blackman, *New Phytologist*, 1921, 20, 2.

⁷² H. A. Spoehr, "The Carbohydrate Economy of the Cacti," Carnegie Inst. Pub. No. 287, 1919.

⁷³ E. C. C. Baly, I. M. Heilbron, and W. F. Barker, *T.*, 1921, 119, 1025.

⁷⁴ W. J. V. Osterhout, *Amer. J. Bot.*, 1918, 5, 511; *A.*, i, 263.

⁷⁵ B. Moore, *T.*, 1921, 119, 1555.

which occur in the leaves of the poplar. It is not difficult in this way to build up substances of any desired degree of elaboration.⁷⁶

Whatever view is taken as to the actual course of photosynthesis, it is known that potassium plays an important part, although there is not necessarily a specific effect. It is shown that wheat can produce and translocate a certain amount of starch in presence of only little of this element.⁷⁷ It does not appear that the potassium is in organic combination in the plant, since it can all be extracted with water.⁷⁸

Iron also has always been regarded as essential for the production of chlorophyll. It is now maintained that the magnesium salt of pyrrolecarboxylic acid serves instead, and in culture solutions determines the formation of chlorophyll even in absence of iron. It is therefore suggested that the function of iron in the leaf is to act as catalyst in the formation of pyrrole, which is regarded as the centre of the chlorophyll complex.⁷⁹

Other inorganic nutrients are essential to plant growth, and special importance has always been attached to nitrogen, potassium, and phosphorus because of the striking results obtained by the use of their compounds as fertilisers. Attempts have been made to find quantitative relationships between the amounts of plant nutrients supplied and of the subsequent plant growth. The old idea that growth was proportional to the quantity of fertiliser had long ago to be abandoned; it was followed by Mitscherlich's view that the effect of a nutrient salt (or other factor) is proportional to the decrement from the maximum obtainable when that salt or factor is present in ample quantity. This view has the merit that it is readily expressible in the form of a logarithmic equation, the constants of which hold out attractive possibilities for the agricultural chemist; it has, however, evoked a storm of criticism in Germany,⁸⁰ and in any case it appears to be too simple a statement, as the results are more readily expressible by a sigmoid than by a logarithmic curve.⁸¹

⁷⁶ P. Mazé, *Compt. rend.*, 1921, 172, 173; *A.*, i, 209. See also *ibid.*, 1920, 171, 1391; *A.*, i, 151.

⁷⁷ T. O. Smith and O. Butler, *Ann. Bot.*, 1921, 138, 189; *A.*, i, 482.

⁷⁸ S. Kostychev and P. Eliasberg, *Z. physiol. Chem.*, 1920, 111, 228; *A.*, i, 83.

⁷⁹ B. Oddo and G. Polacci, *Gazzetta*, 1920, 50, 54; *A.*, 1920, i, 407.

⁸⁰ Among recent papers are A. Mitscherlich, *Landw. Jahrb.*, 1921, 56, 71; B. Baule, *ibid.*, 1920, 54, 493; A. Mayer, *Landw. Versuchs. Stat.*, 1919, 94, 247. For a useful résumé, see E. Lang, *Landw. Jahrb.*, 1920, 55, 337.

⁸¹ Rothamsted Report, 1918-20, p. 14; A. Rippel, *Landw. Versuchs. Stat.*, 1921, 97, 357. For a discussion of the distinction between growth rate and final growth, see C. West, G. E. Briggs, and F. Kidd, *New Phytologist*, 1920, 19, 200.

There has been much discussion, initiated by Shive and Tottingham's earlier work, as to the need for some definite physiological balance between the various plant nutrients; it is, however, shown⁸² that there is no "best" solution for plant growth: a considerable range of mixtures is possible, although "poor" solutions can be made.⁸³

Some proportionality between CaO and MgO seems indicated by consideration of the analyses of plant ash.⁸⁴ A detailed study of the potato in sand cultures is also reported.⁸⁵

Further, it is possible to effect disturbances in plant nutrition by altering the course of absorption of the nutrients. Assimilation becomes abnormal when a plant root is divided among several nutrient solutions from each of which one essential nutrient is withheld. It is suggested that the cause lies not so much with the actual absorption of the nutrient as with the subsequent translocation, and values have been calculated for nitrogen, phosphoric acid, and potassium which show a reasonable measure of agreement with the results actually found.⁸⁶

The older agricultural chemists confined themselves almost exclusively to the three nutrients nitrogen, phosphorus, and potassium; of recent years, however, the French chemists have directed attention to the importance of other elements. Bertrand first insisted on the importance of manganese and now shows⁸⁷ that it is invariably present, the supposed exceptions of Maumené being non-existent. Copper is shown to be invariably present in plants; it is subject to translocation and migrates to points of greatest vitality as if it played an active part in intracellular metabolism.⁸⁸

Iron presents a somewhat more complex problem, since it exists in the plant in two forms which are not readily distinguished: as Fe_2O_3 deposited by evaporation in the leaf or absorbed in the cellular membranes,⁸⁹ and as an organic complex comparable with Bunge's hæmatogen; the latter becomes translocated and moves towards the centres of active life and reproduction.⁹⁰

⁸² A. R. Davis, *Soil Sci.*, 1921, **11**, 1.

⁸³ Confirmed also by L. H. Jones and J. W. Shive, *J. Agric. Res.*, 1921, **21**, 701.

⁸⁴ H. Lagatu, *Compt. rend.*, 1921, **172**, 129; *A.*, **i**, 214.

⁸⁵ E. S. Johnston, *Soil Sci.*, 1920, **10**, 389.

⁸⁶ P. L. Gile and J. O. Carrero, *J. Agric. Res.*, 1921, **21**, 545.

⁸⁷ G. Bertrand and Mme M. Rosenblatt, *Compt. rend.*, 1921, **173**, 333; *A.*, **i**, 759; J. S. Jones and D. E. Bullis, *J. Ind. Eng. Chem.*, 1921, **13**, 524; *A.*, **i**, 840. For a soil study, see P. Nottin, *Ann. Sci. Agron.*, 1920, **37**, 228.

⁸⁸ L. Maquenne and E. Demoussy, *Compt. rend.*, 1920, **170**, 87. See also a suggestive paper by these authors in *Ann. Sci. Agron.*, 1921, **38**, 113.

⁸⁹ For this inorganic iron, see H. W. Jones, *Biochem. J.*, 1920, **14**, 654; *A.*, 1920, **i**, 909.

⁹⁰ L. Maquenne and R. Cerighelli, *Compt. rend.*, 1921, **173**, 273; *A.*, **i**, 759.

A study of iron nutrition has shown that the availability and sufficiency of a particular iron compound depends on the other constituents of the nutrient solution and on its hydrogen-ion concentration.⁹¹ Thus ferric phosphate was of little value to plants when the nitrogenous nutrient was a nitrate; but it was quite effective when ammonium sulphate was used. On the other hand, ferrous sulphate was effective in presence of nitrates, but toxic when used in conjunction with ammonium sulphate.

Pot experiments suggest that small doses of boric acid cause an increase in plant growth, but it is not clear that crop increases are produced in the field. The subject is of some importance in America, because boron occurs in some of the naturally occurring potassium salts which have been proposed for use as fertiliser; it is found that 3 to 5 lb. per acre is the largest permissible dose of anhydrous borax, and there was no evidence of any beneficial effect with this or smaller quantities.⁹²

It is probable that all these effects are complex. Finely powdered sulphur, when added to soil in certain cases, increases plant growth; the action is considered to include at least three factors; some of the sulphur is oxidised by bacteria to sulphuric acid, which brings into solution more phosphate, potassium, etc.; it seems to stimulate the activities of the ammonifying, the nitrifying, and the nodule organisms; and apparently⁹³ it stimulates the production of starch in plants.

Possibly some such action may explain the curious observation that beans germinated and grown in distilled water became etiolated and died for want of food, whilst large reserves still remained in the cotyledons. On the other hand, growth continued in soil and exhaustion of reserves was much more complete.⁹⁴

Plant Constituents.

This branch of the subject belongs properly to organic chemistry, and only brief reference will be made to it here. The fundamental product is starch, but its transformations cannot be followed with certainty because no satisfactory method exists for its determination in plants. Taka-diestase converts it into maltose and dextrose only, and was therefore proposed⁹⁵ as a suitable analytical agent; it now appears,⁹⁶ however, that this substance does not give concordant

⁹¹ L. R. Jones and J. W. Shive, *J. Agric. Res.*, 1921, **21**, 701; *Soil Sci.*, 1921, **11**, 93.

⁹² J. R. Neller and W. J. Morse, *Soil Sci.*, 1921, **12**, 79.

⁹³ G. Nicolas, *Compt. rend.*, 1921, **172**, 85.

⁹⁴ G. D. Buckner, *J. Agric. Res.*, 1921, **20**, 875.

⁹⁵ W. A. Davis and A. J. Daish, *J. Agric. Sci.*, 1914, **6**, 152.

⁹⁶ E. Horton, *ibid.*, 1921, **11**, 240.

results, and indeed doubt is expressed whether any ordinary enzyme would do so. Until he can follow the more important changes in the growing plant, the agricultural chemist is not as a rule directly concerned with questions of constitution of these various constituents.⁹⁷

The nitrogen compounds in plants are steadily being investigated. A method is suggested for extracting the protein from leaves by use of water saturated with ether.⁹⁸

Nitrogen compounds have been extracted and examined from lucerne seed,⁹⁹ pecans, peanuts, and kafir,¹ mungbean² (*Phaseolus aureus*, Roxburgh), coconut³ (*Cocos nucifera*), cohune nut (*Attalea Cohune*),⁴ and the egg plant (*Solanum melongena*, L.).⁵

Some work has also been done on the formation of alkaloids.⁶ Annett⁷ has continued his studies of the morphine content of poppies and has made a survey showing the quantity of opium produced from this crop in the more important districts in India.

That most remarkable of all chemical processes, the synthesis of nitrogen compounds from gaseous nitrogen in the nodules on the clover root, has been further examined but not yet elucidated;⁸ about 60 per cent. of the soluble nitrogen in the nodules of soy bean is precipitated by phosphotungstic acid; apparently, however, no globulin is present and only a small amount of albumin.⁹ Field experiments show the great advantage of inoculation for soy beans, and on certain soils, for canning peas.¹⁰

⁹⁷ Among the papers are: "Starch," M. Samec and H. Haerdtl, *Koll. Chem. Beihefte*, 1920, **12**, 281; A., i, 226; P. Karrer et al., *Helv. Chim. Acta*, 1921, **4**, 678; A., i, 768. "Cellulose," K. Hess, *Helv. Chim. Acta*, 1920, **3**, 866; A., i, 12; P. Karrer and F. Widmer, *ibid.*, 1921, **4**, 174; A., i, 310; M. Samec and J. Matula, *Koll. Chem. Beihefte*, 1919, **11**, 37; A., i, 397; K. Freudenberg, *Ber.*, 1921, **54**, [B], 767; A., i, 400; A. Cleve von Euler, *Chem. Ztg.*, 1921, **45**, 977; A., i, 769. "Wood," H. Wislicenus, *Kolloid Z.*, 1920, **27**, 209; A., i, 84; F. Lenze, B. Pleus, and J. Müller, *J. pr. Chem.*, 1920, [ii], **101**, 213; A., i, 163.

⁹⁸ A. C. Chibnall and S. B. Schryver, *Biochem. J.*, 1921, **15**, 60; A., i, 482.

⁹⁹ H. G. Miller, *J. Amer. Chem. Soc.*, 1921, **43**, 906; A., i, 486; see also next reference.

¹ C. T. Dowell and P. Menaul, *J. Biol. Chem.*, 1921, **46**, 437; A., i, 644.

² C. O. Johns and H. G. Waterman, *ibid.*, 1920, **44**, 303; A., i, 84.

³ D. B. Jones and C. O. Johns, *ibid.*, 291; A., i, 66.

⁴ C. O. Johns and C. E. F. Gersdorff, *ibid.*, 1920, **45**, 57; A., i, 212.

⁵ Kiyohisa Yoshimura, *J. Chem. Soc. Japan*, 1921, **42**, 16; A., i, 296.

⁶ See G. Ciamician and C. Ravenna, *Atti R. Accad. Lincei*, 1920, [v], **29**, i, 416; A., i, 85.

⁷ H. E. Annett, H. Das Sen, and H. Dayal Singh, *Pusa Memoirs Chem. Series*, 1921, **6**, No. 1; H. E. Annett, *Biochem. J.*, 1920, **14**, 618; A., i, 87.

⁸ For further details of the facts, see A. L. Whiting and W. R. Schoonover, *Soil Sci.*, 1920, **10**, 411.

⁹ W. H. Stroud, *ibid.*, 1921, **11**, 123; A., i, 387.

¹⁰ E. B. Fred, *ibid.*, 469, 479.

The function of hydrocyanic acid has been discussed, but no definite conclusion reached.¹¹

Colouring Materials in Plants.

The only colouring material of agricultural interest is indigo, which is still grown to an important extent in India. There is some controversy as to the conditions under which the greatest production of indican is obtained; A. and G. L. C. Howard¹² maintain that the yield is improved by organic manures, but not particularly by superphosphate; whilst W. A. Davis insists that phosphates are of prime importance.

The admirable discussion on colouring materials in plants given by Prof. R. Robinson before the British Association at Edinburgh is of very great interest to agricultural chemists.

Calcifuges and Calcicolous Plants.

Plants which fail to grow on calcareous soils are called calcifuges, whilst those which occur there more frequently than on other soils are described as calcicolous. The cause of the difference is obscure (see p. 197), but a promising mode of study has been opened up by M. C. Rayner,¹³ which offers possibilities considerably in advance of anything hitherto available. A technique has been devised for growing a typical calcifuge *Calluna* and its associated fungus separately in culture solutions. It is shown that *Calluna* will grow normally in an aqueous extract of a non-calcareous soil, whilst it fails to make such good growth in the extract of a calcareous soil. Clearly, therefore, the soil factor concerned is not exclusively physical, since it is transmitted to the extract; it does not appear to be concerned entirely with the reaction, since the favourable extract was neutral and the unfavourable one only slightly alkaline. It should not prove impossible to trace the cause of the unsuitability of the extract of calcareous soil.

Fertilisers.

As in past years, this branch is dealt with fully in the Report to the Society of Chemical Industry, and only brief reference will be made here to features of special interest.

The problem of increasing the supply of organic matter in the soil

¹¹ L. Rosenthaler, *Schweiz. Apoth.-Zeit.*, 1920, **48**, 137; 1921, **49**, 10, 22; *A.*, i, 484; P. Menaul, *J. Biol. Chem.*, 1921, **46**, 297; *A.*, i, 484.

¹² *Pusa Mem. Bot. Series*, 1921, **11**, No. 1.

¹³ M. C. Rayner, *J. Ecology*, 1921, **19**, 60.

has been attacked by ascertaining the conditions under which straw decomposes to form humus, and then carrying out the decomposition on the farm. The necessary conditions are, air and water supply, a nitrogen nutrient for the organisms effecting the decomposition, and sufficient calcium carbonate to ensure neutrality. It is claimed that an effective fertiliser can be produced from straw in this way, and that the process can be worked on farms where insufficient farmyard manure is obtained during the ordinary operations.¹⁴

Much interest has been aroused in technical circles by the announcement in Germany that artificial enrichment of the atmosphere in carbon dioxide was being practised successfully as a means of increasing plant growth both in glasshouses and in the open. A patent has been taken out for absorbing this gas from flue and furnace gases, then evolving it and delivering it in pipes near to the roots of plants. So much interest has been aroused that the method will probably be tested in this country.¹⁵

E. J. RUSSELL.

¹⁴ H. B. Hutchinson and E. H. Richards, *J. Min. Agric.*, 1921, **28**, 398.

¹⁵ F. Bornemann, "Kohlensäure und Pflanzenwachstum," Parey, Berlin, 1920; F. Riedel, *Stahl u. Eisen*, 1919, **40**, 1497; *Möllers Deut. Gärtner Ztg.*, July 20 and 30, 1921, where some illustrations are given; *Chem. Ztg.*, 1920, 585, 808.

CRYSTALLOGRAPHY AND MINERALOGY.

THERE is a very considerable amount of fruitful research in these domains of science to record as the product of the year 1921. After a short respite, during which it appeared as if grave difficulties were accumulating in the path of further progress in elucidating the structure of crystals by means of X-rays, a remarkable step forward has been taken, both as regards new methods and new ground, that of organic chemistry. It will be convenient to commence with the latter most interesting departure first, although its publication has only occurred as this Report is being sent in. By the great kindness of Sir William Bragg, however, the writer was supplied with the proof-sheets, and also had early access to the models.

X-Ray Analysis of Organic Substances.

An attempt had already been made by R. O. Herzog and W. Jancke¹ to obtain information concerning the structure of some organic compounds of the fatty series by means of the X-ray powder method of Debye and Scherrer, but the difficulties met with appear to have been very great, the interpretation of results proving well-nigh insuperable. Cellulose appears to have afforded the least ambiguous results, the elementary monoclinic cell of the space-lattice of the crystals of this substance having been found to contain four dextrose residues, which are of two types, two being of each type.

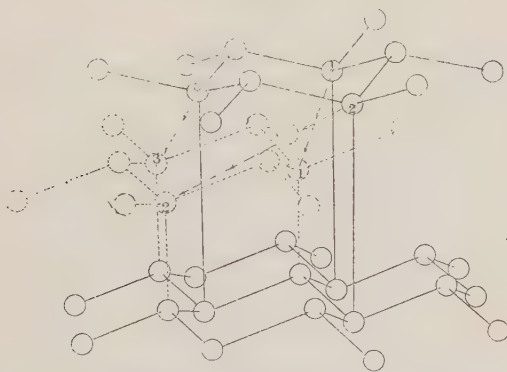
But on November 11th (1921) Sir William H. Bragg,² in his Presidential Address to the Physical Society, which the writer was privileged to hear, announced the first result of a much more successful attack on organic substances, by means of his own methods of X-ray analysis. He was led to begin with a few of the better crystallising aromatic compounds, especially naphthalene and its derivatives, and for a reason which in itself is highly interesting. It will be remembered that the elucidation of the structure of the diamond was one of Sir William's early successes, and sub-

¹ R. O. Herzog and W. Jancke, *Z. angew. Chem.*, 1921, **34**, 385; *A.*, ii, 531.

² Sir W. H. Bragg, "The Structure of Organic Crystals," *Proc. Phys. Soc.*, 1921, **34**, 33.

sequently Debye and Scherrer, and independently A. W. Hull, discovered the structure of graphite, by means of the powder method, and found it to be a trigonal one which is illustrated by the model of which a drawing is shown in continuous line in Fig. 1. Now the remarkable thing is, that if the top layer of the model be moved to the closer and rotated position indicated by the dotted lines, the structure of the diamond is obtained. It will be recalled that in diamond the carbon atoms are arranged on a face-centred cube lattice, with also an atom in the centre of every alternate one of the eight cubelets into which the main cube is divided. It thus consists of a series of puckered layers parallel to any given plane of the tetrahedron, and each carbon atom is attached to four others. The diamond cleaves along these layers.

FIG. 1.



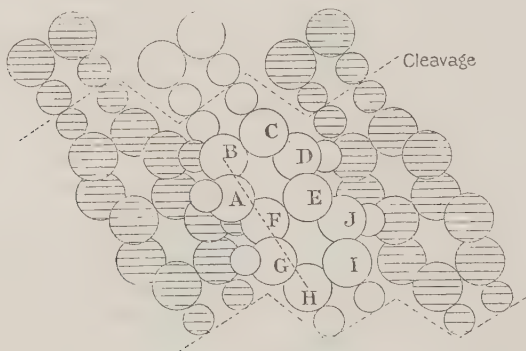
Conversion of Graphite to Diamond Structure.

The structure of graphite shown in Fig. 1 is conversely afforded by taking two such layers of the diamond model and moving one of them away from the other, to the position corresponding to that in Fig. 1. The exact configuration shown, in which the lines are puckered, is that given by Hull, whereas Debye and Scherrer place them in the same plane. Whether puckered or plane, however, these layers are clearly composed of six-carbon-atom rings. Now the very strong bonds between the atoms of these rings in the layers of a diamond not only persist in the graphite structure, but are drawn somewhat tighter, while the distance separating the layers in the latter is much greater than in the more symmetrical diamond; the cohesion is thereby so much lessened between the layers that graphite is one of the softest of substances, not only splitting readily in layers, but actually being useful as a lubricant. On the other hand, diamond is the hardest substance known. The

shortest distance between each pair of carbon atoms lying in the same layer in the diamond is $1.54 \text{ \AA.U.}$, while in graphite it is shortened to 1.50 ; but the distance between two successive layers is increased by $1.35 \text{ \AA.U.}$, so that a carbon atom in graphite is now equally distant from its three nearest neighbours of the next layer, namely, by the relatively large amount of $3.25 \text{ \AA.U.}$, according to Hull.

These interesting facts regarding elementary carbon have caused Sir William Bragg to believe that the hexagonal rings, which persist even in graphite, do so also throughout the aromatic compounds. He therefore assumes the benzene ring to be such a simple hexagonal ring, more or less puckered, of carbon atoms, whilst naphthalene is composed of double rings, and anthracene of triple rings. Using Hull's spacings, the arrangement in naphthalene he

FIG. 2.



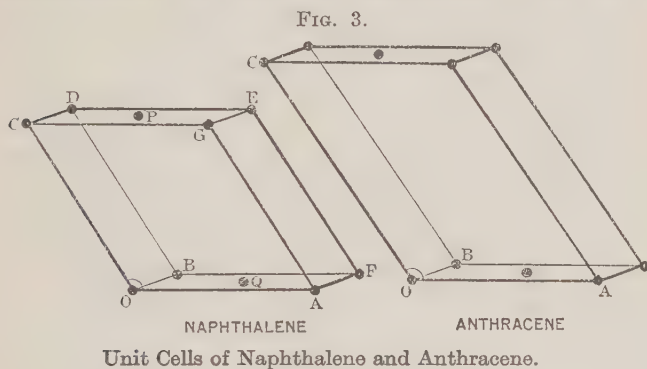
The Structure of Naphthalene.

considers to be that shown in Fig. 2, which includes three naphthalene molecules and parts of others. The ten carbon atoms, from *A* to *J*, form the double ring corresponding to one molecule of naphthalene, while the six atoms *A B C D E F* form a benzene ring. The centres of the atoms *A* and *G* are $0.71 \text{ \AA.U.}$ above the plane, and the centres of *D* and *J* the same distance below the plane of the diagram, those of the rest of the atoms lying in the plane itself.

Benzene is not an easy substance on which to commence the attack, as it is only solid below 6° , its melting point. It is interesting to recall, however, that Debye and Scherrer believed that they had obtained evidence that the molecule of benzene has the form of a hexagonal tablet, the edge of the regular hexagon having the length $6.02 \text{ \AA.U.}$, and the thickness of the tablet being $1.19 \text{ \AA.U.}$ Naphthalene, C_{10}H_8 , crystallises in the holohedral, prismatic, class 5

of the monoclinic system, possessing both the digonal axis of symmetry and the plane of symmetry perpendicular to it, the ratio of the axes being $a : b : c = 1.3777 : 1 : 1.4364$, and the axial angle β being $122^\circ 49'$. The very perfect cleavage is parallel to the basal plane (001), and the other principal faces developed are (110), (20 $\bar{1}$), and (11 $\bar{1}$). The density is low, 1.152.

The first results afforded by the X-ray spectrometer indicate that the space-lattice of both naphthalene and anthracene is No. 13, the unit cell of which consists of a parallelepipedon with two pairs of rectangular faces, inclined at the axial angle β , and one pair of rhomboidal ones, as shown by the two cells in Fig. 3, the dimensions for naphthalene being $a = 8.34$, $b = 6.05$, $c = 8.69$ Å.U. It was next found that two molecules are contained in each cell, the knowledge being derived in the usual Bragg manner from the density,



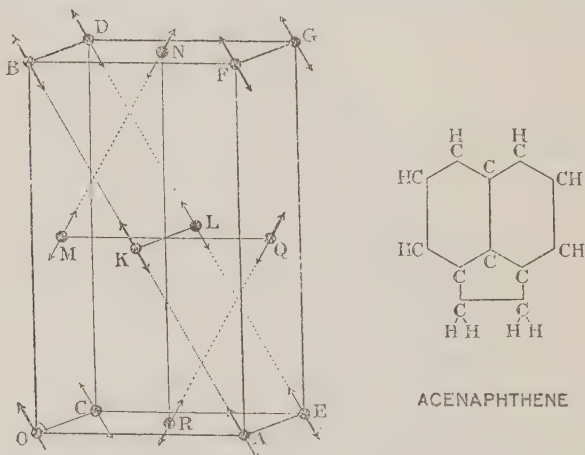
the actual weight of the molecule, the axial ratio, and the X-ray measurements; for it was found that the (100) and (010) spacings are only half what they should be if each corner of the cell represented a single molecule; for only one-eighth of a corner molecule is assignable to this particular cell, each corner being the point of contact of eight adjacent molecules, so that the whole eight parts correspond together to one whole molecule within the cell. But the spacing of (001) agrees, so there must also be a molecule at each of the points P and Q in Fig. 3, each contributing half a molecule to the cell.

On proceeding next to anthracene, $C_{14}H_{10}$, the crystals cannot be used similarly for the single crystal method, as they are only small flakes; but by pressing a number of them against a flat disc, so that all their (001) planes were parallel thereto, a determination of the (001) spacing was found possible, and the linear dimensions of the unit cell were determinable. The crystallographic axial ratio of anthracene is $a : b : c = 1.4220 : 1 : 1.8781$, the axial angle

is $124^{\circ} 24'$, and the density 1.15. There were found to be two molecules to each unit cell, as in the case of naphthalene, and the dimensions afforded by the *X*-ray measurements were $a = 8.7$, $b = 6.1$, and $c = 11.6$. These values, as regards a and b and the axial angle, were nearly the same as for naphthalene, but the c -length was $2.9 \text{ \AA.U.}$ greater.

Now this result is of the greatest importance, for if we accept that the double-ring naphthalene molecule at each corner is replaced by the three-ring molecule of anthracene the increase in size should be about $2.5 \text{ \AA.U.}$ per molecule. Sir William Bragg concludes, therefore, that the double- or triple-ring molecules lie along the vertical c -axis, and that the anthracene cell is longer than that

FIG. 4.



Unit Cell and Constitutional Formula of Acenaphthene.

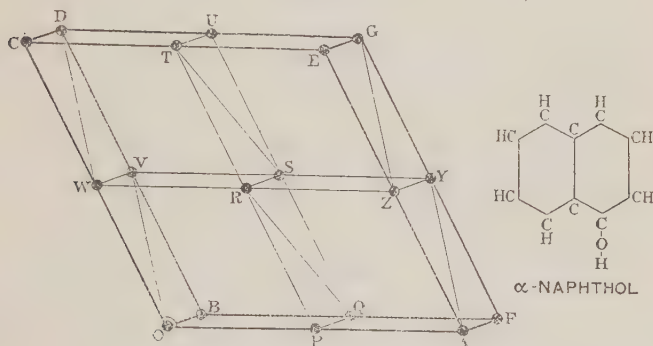
of naphthalene by the observed amount for this reason. The lengths of the molecules of the two hydrocarbons, without allowing for the hydrogen atoms, are 6.41 and $8.86 \text{ \AA.U.}$ respectively, so that there is a vacant space between the ends of the molecules for the accommodation of the two β -hydrogen atoms. As regards the position of the plane of the double- or triple-ring molecule, which must contain the c -axis, all the indications point to the probability that it approximates to the (010) symmetry plane ac , that the β -hydrogens of one molecule lie up against the corresponding ones of the next molecule, and that the (001) plane passes through them all. This (001) plane is then naturally the plane of cleavage, as is actually observed, the atoms being condensed and strongly attached in the rings in the plane, and the cohesion a minimum in the perpendicular direction. The α -hydrogen atoms, those on the sides

of the double- or triple-ring molecule, lie up against the carbon atoms of the neighbouring molecules, and there is about 1 Å.U. of space for them, an adequate amount.

The forces between the molecules are weaker than the valency forces, and of these weaker forces those between the β -hydrogen atoms are weaker than those between the α -hydrogen and carbon atoms. But these two weaker sets of forces are those which bind the molecule into the crystal. The structure thus arrived at is a very open one, as will be clear from Fig. 2, in which the smaller circles represent the hydrogen atoms.

Three derivatives of naphthalene have also been studied, acenaphthene and the α - and β -naphthols. A most interesting result has been afforded by acenaphthene, the structure and constitution

FIG. 5.

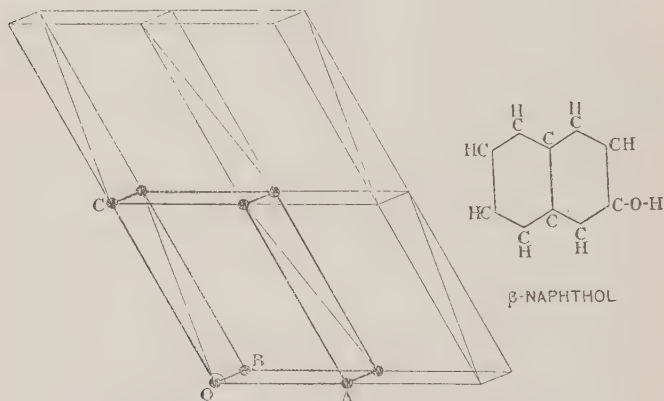


of which are shown in Fig. 4. While the molecule has been made lop-sided by the substitution of 2CH_2 for the two hydrogen atoms on one side, the crystal itself is of higher symmetry than that of naphthalene, being holohedral orthorhombic (class 8), with the axial ratio $a : b : c = 0.5903 : 1 : 0.5161$. The X-ray analysis has shown that there are in this case not two but four molecules in the unit cell of the space-lattice, the sides of which have the absolute lengths $a = 8.32$, $b = 14.15$, and $c = 7.26$ Å.U. In fact, the enhancement of the symmetry, compared with that of naphthalene, has been produced by two of the four unsymmetrical molecules being arranged mirror-image-wise with respect to the others, across one of the principal planes. There is a molecule at each corner of the cell, and also one in the middle of each face. Those at the corners and also those at K and L lie parallel to AB , while those at M , N , Q , and R , which between them contribute to the cell the other

two molecules which belong to it, slope the other way, parallel to MN , while lying in the same plane.

Considering now α -naphthol, this substance forms monoclinic crystals of the holohedral prismatic class 5 like naphthalene, with an axial ratio of $a : b : c = 2.7483 : 1 : 2.7715$, and an axial angle $117^\circ 10'$. Its density is 1.224. There are found to be four molecules in the unit cell, which has the absolute dimensions $a = 13.1$, $b = 4.9$, and $c = 13.4$ Å.U., and which is represented in Fig. 5. These lop-sided molecules are placed as shown in the figure, and they lie with their double-ring lengths "criss-cross," as represented by the diagonal lines, but they now lie edge-ways on top of one another instead of flat-ways, the a -axis and not the c -axis running

FIG. 6.

Unit Cell and Constitutional Formula of β -Naphthol.

along the line of crossings. The cleavage plane, however, again passes through the β -junction. The hydrogen atoms fit very naturally into their places, and link the tops of the molecules together in one (001) layer and the bottoms in the next layer. The hydroxyl groups are thus brought rather close to each other, as if the attraction were between the oxygen atoms.

It has only been possible to investigate the powder of β -naphthol, but this has been adequate to fix the absolute dimensions of the monoclinic space-lattice unit cell. Fig. 6 shows this lattice and also the constitutional formula. The axial ratio is $a : b : c = 1.3662 : 1 : 2.0300$, and the axial angle $119^\circ 48'$. The cell dimensions are $a = 5.85$, $b = 4.28$, and $c = 8.7$ Å.U. It is found that only one molecule goes to a cell, but it is the small (quarter) cell indicated by strong lines in the figure. The removal of the hydroxyl group from the side to the end of the molecule has caused

the cell to shrink in its lateral dimensions and to grow along the vertical axis, thus affording a striking confirmation of the assumption that the molecules lie lengthwise along the vertical *c*-axis. The cleavage plane still cuts along the β -hydrogen junctions. This quarter cell, however, does not account for the full symmetry, for the dissymmetry of the single molecules would lower the crystallographic symmetry; the four cells containing together four molecules, as in α -naphthol, are requisite to account for the holohedral symmetry of the crystal, and so the large cell of the figure, containing four molecules, is to be considered as the unit cell of the space-lattice, the "grosser unit" of the crystal structure as the writer terms it, exhibiting the true symmetry of the crystals of the substance in question. The hydroxyl groups are drawn together, so that pairs of molecules point opposite ways. The structure is thus essentially similar to that of α -naphthol.

A more limited study was found possible of α -naphthylamine, a unit cell of almost exactly the same rectangular shape and dimensions as acenaphthene being revealed, which contains four molecules and has the dimensions $a = 8.62$, $b = 14.08$, $c = 7.04$ Å.U., but a and c are interchanged in the two substances. The length of the molecule works out to be: for α -naphthylamine 8.25, for acenaphthene 8.23, and for α -naphthol 8.31. The lop-sided molecules in all three cases are laid criss-cross on one another, whereas in naphthalene itself they are arranged parallelwise, and the somewhat different length, 8.7, of the naphthalene molecule is a consequence.

Until benzene itself has been investigated, which will involve special low-temperature arrangements, the well-crystallising benzene derivatives cannot be fully worked out, but as regards benzoic acid it has been established that the (001) spacing is quite exceptionally wide, 10.9 Å.U., and that sheets of molecules lie in these (001) planes at this wide distance apart, the dimensions of the cell, which contains four molecules, being $a = 5.44$, $b = 5.18$, $c = 21.8$ Å.U., and the axial angle $97^\circ 5'$. Moreover, the sheets differ alternately, and the bridging appears to occur by the COOH extended groups, a CO extension from one ring probably joining on to an OH extension from another ring. These bridges, however, are very flimsy, and the crystals consequently flake at the least touch. The powder method had to be used because of this property.

The Bearing of these New Results on Molecular Structure.

These interesting results with aromatic organic substances are considered by Sir William Bragg to agree extremely well with the work of Langmuir. The forces that bind atoms together are clearly shown to be of more than one kind. The very strong valency

bonds, whether due to electron sharing or other causes, are exemplified by all the linkings between the carbon atoms of the diamond, and also by those in the planes of the flakes of graphite. Quite different, however, are the much weaker bonds between an atom in one graphite sheet and its three nearest neighbours in the next sheet. It is this weaker second kind of bond which unites the molecules of the organic compound so as to form the crystal. The cleavage is the indication of their weakest direction. These weaker bonds are definitely associated with special points on the molecule.

"When a crystal forms in a liquid, or by sublimation, the molecule that attaches itself correctly, and with proper orientation to others already in position, is the one that stays there and resists the tendencies of other drifting and thermally agitated molecules to remove it. It is fixed by the attachment of certain points on its own structure to certain points on the structure of the other molecules. The beautiful exactness of crystal structure is evidence of the precision with which this adjustment is made; and at the same time of the definite molecular form without which precision would be impossible."

In the case of naphthalene the molecules arrange themselves side by side, the α -hydrogens of each molecule seeking to attach themselves to the carbon atoms of its neighbours, no valency bonds being concerned. This side-to-side combination is preferred to the end-to-end attachment, so that a crystal grows quickly out into thin sheets. Moreover, the particular geometry may permit a molecule to attach its active points to those of other molecules in more than one way, producing twinning rather than a continuation of the previous regularity.

The surface films studied by Langmuir, Adam, and others were not aromatic compounds, but they exhibited similarly strong side-to-side attachments of their molecules as compared with end-on attachments. A film of oleic acid, for instance, is formed on water when the hydroxyl ends of some of the molecules root themselves in and are held quietly by the water, while other molecules link on side by side and the film thus spreads over the water. The arrangement parallelwise of the long-chain molecules, the swarm of Bose, of the substances forming the "liquid crystals" of Lehmann is probably similar, ammonium oleate, $C_{18}H_{33}(NH_4)O_2$, being one of the best known cases, the length of the molecules themselves in these long-chain compounds facilitating the process.

Sir William Bragg finally concludes that "the arrangement of molecules in crystals . . . cannot be fully explained as due to forces which are merely functions of the distances between their centres. Confining ourselves to cases where there is no obvious separation

of electron charges, as there is none in the crystals described above, it is clear that we must think of molecules as bodies of very definite form. These attachments to one another are made at definite points, and the forces there exerted may have very short ranges. The molecules are locked into crystal structure when attachments are made at sufficient points, and the whole has the stability of an engineering structure."

This very clear result of Sir William Bragg's work on the aromatic carbon compounds will materially assist in correcting the very premature statements that have been made by some authors, even by Prof. von Groth, soon after the first results of X-ray analyses of very simple binary compounds and elementary substances were published, that chemical molecules do not exist in the crystalline condition.

The present writer³ has felt impelled to protest strongly against this very improbable conclusion, and has pointed out that "there can be no question but that the growth of a crystal is to be attributed to the special properties of the surface of the solid crystal already laid down, whereby further accretions of growth occur," and that "the whole process of the passage from liquid to crystal is so continuous, and the natural succession of phases—gas, liquid, liquid crystal, and true solid crystal—follow so unbrokenly, that to deny the continued existence of the molecule at any stage is illogical.

"The fact that the persistence of the molecule is not absolutely essential to the geometrical explanation of crystal structure is not a valid argument for denying that persistence. . . . The close approximation of the molecules in the act of crystallisation may yet occur without destruction of the interatomic forces which retain the molecules as such. There may be a certain amount of pooling of the chemical affinities when the atoms are brought into such close neighbourhood that those belonging to different molecules are little if any further removed from each other than those of any one and the same molecule; indeed it is likely that these forces exerted at close quarters by the atoms of one molecule on those of other approaching molecules together constitute the directive force of crystallisation, which determines the type of crystal structure produced. In any case, at the first opportunity, such as that afforded by solution or fusion, for instance, the same molecules or others indistinguishable from them are again restored as freely moving separate entities. Also only concentrated, indeed supersaturated, and not dilute, solutions are concerned in crystallisation, so that electrolytic dissociation and ionisation are excluded."

³ A. E. H. Tutton, "Crystallography and Practical Crystal Measurement," 2nd edition, now on point of publication, Macmillan and Co.

These views, written before Sir William Bragg's work on the aromatic compounds was carried out, are thus remarkably verified by the results of this important research. It may also be recalled that in the Report for 1914 written by Mr. T. V. Barker (page 247) it was very truly observed that to deny the existence of the chemical molecule in the solid crystalline state would open up most extensive possibilities of isomeric change, optical inversions, and so forth, whenever the crystal structure is broken down by dissolving the solid in a solvent or by subjecting it to fusion. That such changes have never been observed is a strong argument in support of the view of the persistence of the molecule throughout.

The writer was much impressed with the prevalence of misconception on this subject when listening to the discussion which followed Dr. Irving Langmuir's address at the Edinburgh meeting of the British Association in September last (1921). Several speakers referred to Prof. Arrhenius, the distinguished exponent of electrolytic dissociation in dilute solution, who was present, as having now taken over also crystals under his wing. The misconception has doubtless arisen from the fact that in such a simple case as potassium chloride the crystal may be regarded as an assemblage of potassium and chlorine "ions" arranged on a cubic lattice, in which each ion is surrounded by six ions of the opposite sign, and that there are no individual molecules recognisable in the crystal structure, the potassium ion having exactly the same relation to the six chlorine ions surrounding it, and vice versa.

In such very simple compounds the pooling above referred to is at its maximum, and the lack of any necessity for assuming molecular persistence is obvious. The meaning here attached to the word "ion" is not, however, that used in electrolytic dissociation. To generalise from such a simple case as potassium chloride is in any case dangerous, and Sir William Bragg now shows that for more complicated compounds such as naphthalene the generalisation is untrue, and that the molecule is not only persistent but remains remarkably intact, not only in the parent substance but (with the substitutions or replacements) in all its derivatives, and that two or four such intact molecules form the unit cell of the space-lattice, that is, furnish what the writer calls the grosser unit of the crystal structure, that which exhibits all the symmetry characters of the crystals.

The real meaning of the "ionisation" intended in the case of sylvine is clearly explained by Prof. W. L. Bragg,⁴ as well as by Dr. Langmuir. The atom of potassium, atomic number 19, has a nuclear charge of 19 positive units, and is surrounded by 19 negative

⁴ W. L. Bragg, *Phil. Mag.*, 1920, [vi], **40**, 182, 183; *A.*, 1920, ii, 537.

electrons, of which 18 are arranged as in argon, in three complete shells and one extra electron outside this stable arrangement. Chlorine, atomic number 17, has a nucleus with a charge of 17 positive units surrounded by 17 electrons, one less than the number required to form the stable argon arrangement. The combination of potassium and chlorine is effected by the chlorine atom absorbing the extra (19th) electron of the potassium atom, to complete a stable argon shell system on its own atom. The nuclear charges remaining 19 and 17, however, but each atom having now 18 electrons, the resultant charges are a one-unit positive charge on the potassium atom and a one-unit negative charge on the chlorine atom; the two atoms, therefore, attract each other electrostatically and form the molecule KCl. The nuclei surrounded by their stable argon shells are regarded as univalent kations and anions of potassium and chlorine respectively. This is the precise sense in which these "ions" in crystal structure are to be understood. It is supposed that the electrostatic force which would otherwise cause the formation of individually recognisable molecules as just described is prevented by some repulsive force between the outer shells, which keeps the atoms apart, and causes their arrangement in the cubic lattice, so that any one ion is surrounded by six of the opposite kind.

The fact that the greatest stability is attained in the solid crystal when this lattice arrangement obtains is not itself, however, a proof of the accuracy of the no-molecule theory, and as molecules are present in the supersaturated solution or liquid just before crystallisation (when approaching to form the solid), and certainly when the crystal is again taken down by solution or fusion, this no-molecule theory appears to the writer superfluous. The naphthalene results will in any case require its revision.

With regard to the repulsive force which counterbalances the electrostatic attraction (and which has been so insisted on by Kossel), and thus keeps the "ions" apart, it is probably due to the electronic movements assumed by Born and Landé. Indeed the latter, in his latest paper,^{4a} assumes that not only the atomic nucleus, but also the corresponding electrons of all like atoms form a lattice, which oscillates about the stationary nuclear lattice, thus guaranteeing the regular structure of crystals.

The further investigation of crystals by means of X-rays during the year 1921 has resulted in the extension of the Bragg spectro-metric method to (a) the adaptation of the powder method of Debye and Scherrer and of Hull to the X-ray spectrometer, (b) the more detailed study of the intensity of X-ray reflection of the

^{4a} *Z. Physik*, 1921, **3**, 410.

different orders at a given crystal facial plane, and (c) an attempt to locate the exterior electrons of the atom.

Application of the Powder Method to the X-ray Spectrometer.

With respect to (a) it should be made clear that there are two distinct methods of using the X-rays for crystal investigation. In one, the original method, a single crystal is employed, and the experience now acquired shows that the relatively large size of crystal employed during the early work is by no means essential; the crystal need not weigh more than a few milligrams, and it is actually more convenient that it should be small, for the pencil of reflected rays is then conveniently limited without the need for slits other than to act as stops. This method is still the best and most valuable and instructive.

The other method, in which crystal powder is employed, is of great value when good, small, isolated crystals are not available. All the spectra from the different planes of atoms effective are thrown together on the same photographic film or plate, and require to be disentangled, a process which has been much simplified by Sir William Bragg. Instead of using the cylindrical camera of Debye and Scherrer, at the axis of which lies the cylindrical tube or capillary containing the crystal powder, he pastes the powder on a flat surface and places the latter, instead of the crystal, on the X-ray spectrometer. A Muller X-ray bulb is most suitable for use with this method, actuated by a half-kilowatt transformer. The spectrometer slit is brought close up to the radiator, becoming thereby the source of a very powerful beam of X-rays sufficiently divergent to cover a relatively large surface of the plate on which the powder is spread. The anticathode is preferably of copper, as the long wave-lengths of the copper *K*-series of X-rays give suitable angles of deflection even for the wide spacings that are found in organic crystals. The method is especially suitable for organic crystalline substances, many of which can only be obtained in very small, flaky, acicular, skeletal, or otherwise imperfect forms, useless for the single crystal method.

The Interpretation of Intensity of X-ray Reflection.

The very difficult question (b) of the correct determination and interpretation of the intensity of X-ray reflection in the different orders, from a plane of atoms in a crystal, has been specially investigated by Prof. W. L. Bragg,⁵ in collaboration with R. W. James

⁵ W. L. Bragg, R. W. James, and C. H. Bosanquet, *Phil. Mag.*, 1921, [vi], 41, 309; 42, 1; *A.*, ii, 477.

and C. H. Bosanquet. Very purely homogeneous X-rays were first obtained, by preliminary reflection, from a crystal of rock-salt, of the rays from an already fairly pure source, such as the 0.584 Å.U. radiation from a palladium anticathode. A diagram of the arrangement is given in Fig. 7. Such preliminary reflection (from the crystal C_1) at the correct glancing angle eliminates all other undesirable general radiations, and the intensity of the very pure ray thus obtained can be measured with considerable accuracy. When this pure ray of known intensity is allowed to fall on the crystal under investigation C_2 at the proper glancing angle for that crystal the reflected beam can be investigated as to its exact intensity with great confidence. The ray is directed exactly to the first crystal face C_1 by the leaden wedge W , round which the reflection occurs; and the second crystal C_2 is rotated with uniform velocity, and the total amount of radiation reflected is measured in the usual way. From a considerable amount of experimental work on these lines, using rock-salt and a number of other suitable well-crystallised substances, a formula of a comprehensive character has eventually been derived, as the expression of the reflecting power of a crystal plane. It includes factors due to the work of Debye and Scherrer, Darwin and Compton, and of Sir W. H. Bragg, derived both from theoretical considerations and from exact measurements. It is as follows:

$$R = \frac{N^2 \lambda^3}{2\mu \sin 2\theta} \cdot F^2 \frac{e^4}{m^2 c^4} \cdot \frac{1 + \cos^2 2\theta}{2} \cdot e^{-B \sin^2 \theta},$$

in which R is the reflecting power of the face (plane of atoms), N is the number of atoms per unit volume, λ the wave-length of the X-rays, θ the glancing angle of reflection, μ the linear absorption coefficient of the X-rays in the crystal substance, e the charge and m the mass of an electron, c the velocity of light, B a constant determined by Sir William Bragg to be 4.12, and F a factor depending

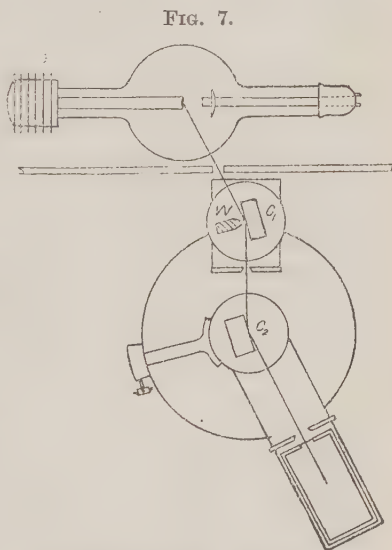


FIG. 7.

Arrangement for Determination of
Intensity of Reflected X-rays.

on the angle of scattering and the number and arrangement of the electrons of the diffracting atom. This interesting factor F has its maximum at a very small angle of scattering and falls off as the glancing angle increases, owing to interference between the wave-trains diffracted by separate electrons. By comparing the theoretical formula with the measurements obtained by experiment it is possible, since all the other constants are known, to determine this factor over a range of angles, and thus obtain valuable information concerning the arrangements of the electrons in and around the atom, and in particular concerning the positions of those composing the outer shell.

The results as published in the two papers quoted agree with the Lewis-Langmuir version of the atomic structure theory. The experimental work with sodium chloride, for instance, afforded measures of the intensity of reflection of (amplitude of the X -rays diffracted by) the chlorine and sodium atoms separately over a range of angles from 10° to 60° , and also indicated the correct number of electrons in the atoms of each element, and that they are distributed in shells. In a contribution to the discussion on Dr. Langmuir's address to the British Association in September (1921), however, Prof. Bragg stated that the distribution indicated was one in which the inner shells of electrons were somewhat closer to the nucleus than was expected.

Attempt to Locate Exterior Electrons of Atoms.

The third new departure (c) is of a still more fascinating character, the direct application of the X -ray spectrometric method to the location of the outer electrons of the atom, thus even more directly experimentally than as described under (b) going beyond the crystal structure to that of the atoms composing it. The work is described in two papers by Sir William H. Bragg⁶ and Mr. H. Pealing.⁷ Sir William Bragg, and also Debye, had for some time been considerably exercised as to the existence or otherwise of a weak second order spectrum from the tetrahedral planes of the diamond, but at last Sir William has definitely observed it. The fact is of great importance as it determines that alternate planes of carbon atoms are not alike, and that the carbon atom has in itself a tetrahedral arrangement of electrons, and not a sphere with similar properties in every direction from the centre, but is tetrahedrally differently disposed, as if there were connecting electrons thus arranged between the atoms. This further implies something tetrahedral in the atom itself, for the electrons to fit on to.

⁶ Sir Wm. H. Bragg, *Proc. Phys. Soc.*, 1921, **33**, 304.

⁷ H. Pealing, *ibid.*, 297.

Mr. Pealing studied fluorspar in a similar manner and obtained analogous results. It will be remembered that the calcium atoms occupy the points of a face-centred cube lattice, and the fluorine atoms the centres of the eight cubelets into which the calcium cube may be divided. As the atomic weight of calcium (40) almost exactly balances the weight of two fluorine atoms ($2 \times 19 = 38$), the first-order spectrum from the cube planes is nearly extinguished. But the third-order, instead of being still more completely neutralised, is much more intense, indicating the presence of some weak diffracting centre about one-third or one-fourth of the way between calcium and fluorine planes, and these appear to be singularities at the points of junction between the calcium and fluorine atoms, probably connecting electrons.

Hence, these experiments clearly point to the existence of stationary electrons, or at least of electrons having average positions which are not central but have other definite stations. Further, they show that the atoms in the crystal are not packed into the smallest possible volume, but form a structure in which relatively large empty spaces are left. In the case of the diamond each atom is surrounded by only four neighbours, whereas there would be twelve in the close-packed arrangement of similar atoms; indeed, the structure is so hollow that an additional equal number of atoms could be accommodated in a given space, the arrangement then becoming that of the centred cube, in which each atom has eight neighbours.

These results are also in agreement with the Lewis-Langmuir version of the atomic structure theory. For the carbon atom of the diamond is shown to have four special directions or positions of attachment of one atom to the next, corresponding with its quadri-valency. And as regards fluorspar, the results agree with the supposition of Langmuir, on the same principle as already explained for sylvine, that a calcium atom of atomic number 20 has two extra (valency) electrons above the 18 needful to form the stable argon shell of 18 electrons, and will thus combine with two fluorine atoms of atomic number 9, having one electron each less than required to form the stable neon arrangement of 10 electrons, to produce a compound having the stable shells corresponding to argon and neon around their nuclei.

All this recent crystallographic X-ray work is thus so intimately bound up with the Lewis-Langmuir generalisation that it is essential that a brief account should here be given of the relevant portion of Dr. Langmuir's address to the joint Chemical and Physical Sections of the British Association at the late (September 1921) Edinburgh meeting.

The Lewis-Langmuir Theory as expounded by Dr. Langmuir.

The writer, who was present on the occasion, gathered that there are three main assumptions. The first is that the electrons in atoms surround the nucleus in successive layers, shells, or sheaths containing 2, 8, 8, 18, 18, and 32 electrons respectively, their ratio being as $1^2 : 2^2 : 2^2 : 3^2 : 3^2 : 4^2$. The second is that atoms may be coupled together by one or more "duplets," or pairs of electrons, held in common by the completed sheaths of the atoms. The third is that the residual charge on each atom and on each group of atoms tends to a minimum.

Experimental evidence was given by Dr. Langmuir, such as that derived from vapour-density determinations of the liquid carbonyls, that the number of electrons in the various shells is as given above and not that assumed in the Bohr-Sommerfeld version (2, 8, 18, 32, 18, 8). It was also pointed out that the sharing of a duplet (pair) of electrons by two atoms corresponded to what has become known as co-valency, and that this kind of bond is that met with, for instance, in the organic compounds; and that the bonds chiefly met with in inorganic compounds are those of electro-valency, supposed to be due to an electron or electrons passing from the sheath of one atom to that of another. The first type indeed (which shares electrons) usually occurs between two electro-negative elements, and the second type between an electro-positive and an electro-negative element. A chemical combination is represented in general form by Dr. Langmuir by the equation

$$\Sigma v_e + \Sigma v_c = 0,$$

where v_e is electro-valence and v_c is co-valence: also $v_e = e - s$, where e is the kernel (nuclear) charge and s is the number of electrons in the complete sheath, 8, 18, or 32.

Dr. E. K. Rideal pointed out that the very opposite assumptions of a static character in the Langmuir atom, and of a dynamic character in the Bohr atom, may be reconciled by regarding the atoms as static except during the actual emission or absorption of energy, oscillation of the electrons under these conditions being more probable than rotation. Indeed there is a general feeling prevalent that eventually the Lewis-Langmuir and Bohr-Sommerfeld versions of the atomic structure theory will be brought together, and give us between them a fuller expression of the truth. The history of science is rich in such cases. It would even appear as if an important step in this direction has been taken by Sir J. J. Thomson in his latest paper (*Phil. Mag.*, 1921, [iv], **41**, 510), in which he shows that his results agree with the law of atomic diameters of

W. L. Bragg, and with Langmuir's version so far as the character and number of electrons in the outer shells are concerned. But no sharing of electrons is assumed, molecules being supposed to be formed by the outer electrons simply acting as couplings, each valency bond requiring two electrons, one belonging to each atom, and a double bond being formed by four electrons arranged at the corners of a square at right angles to the line joining the atomic centres. These views appear to offer a good explanation of the benzene ring, and are favourably received by many organic chemists.

Prof. A. O. Rankine adduced some interesting facts in support of Dr. Langmuir's assumptions, from his experimental determinations of the viscosity of gases. In the first place his results lead to a diameter of the chlorine molecule which is practically identical, as it should be according to the Langmuir version, with the added diameters of two argon atoms, the outer shells of which are in contact; also to similar results with respect to bromine and krypton, and with regard to iodine and xenon. In the second place, a remarkable additional significance was pointed out, of the fact discovered by the present writer during the course of his crystallographic investigation of isomorphous series (sulphates, selenates, and double salts), namely, that analogous ammonium and rubidium salts are practically isostructural, their molecular volumes and the dimensions of their space-lattice unit cells being almost exactly the same. Rankine assumes, therefore, from this fact that rubidium and ammonium possess equal molecular volumes, and that if the Langmuir version be correct krypton should bear the same relation to rubidium as methane, CH_4 , bears to ammonium, NH_4 , and an atom of krypton should have the same volume as a molecule of methane. Actual determinations by Rankine of the volumes of krypton and methane by the viscosity method agree with this precisely.

It is of more than merely passing interest that this fact of the isostructure of the rubidium and ammonium compounds should prove of such use. The fact has been verified over and over again during the course of the writer's work, no less than eighteen cases having been studied; and it is confirmed once more in the final instalment, on the manganese and cadmium groups, of the research on the double selenates, which the writer has just completed, so that no exceptions for the oxy-salts (sulphates, selenates, double-sulphates, -selenates and -chromates) are now possible. It was fully substantiated by the absolute measurements made with the writer's crystals in Sir William Bragg's laboratory by Prof. A. Ogg and Mr. F. L. Hopwood ⁸ of the space-lattice cells of ammonium and

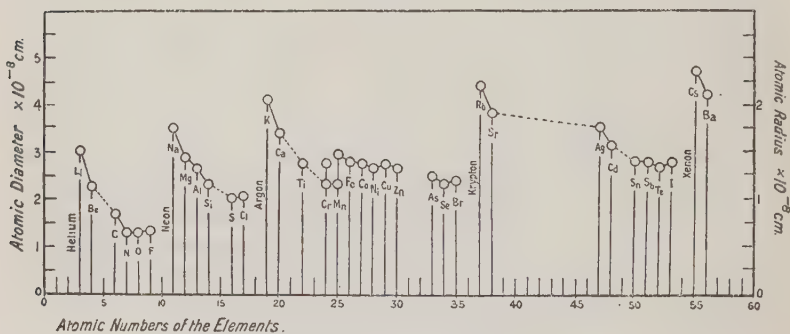
⁸ A. Ogg and F. L. Hopwood, *Phil. Mag.*, 1916, [vi]. **32**, 518; *A.*, 1916, ii, 594.

rubidium sulphates. It was this same fact which afforded conclusive evidence of the fallacy of the valency volume theory of Sir William Pope and Mr. W. Barlow; for if that theory were correct the volume of the ammonium sulphate cell should be twice that of the unit space-lattice cell of rubidium sulphate. The law of atomic diameters of Prof. W. L. Bragg, which affords the true sizes of the atoms, and is so fully confirmed by the work of Rankine, now replaces the theory of Pope and Barlow, and with this law the writer's results for isomorphous series are in complete agreement.

Bragg's Law of Atomic Diameters.

This law, which had only just been announced by Prof. W. L. Bragg⁹ when last year's Report was written, and could be only

FIG. 8.



The Curve of Atomic Diameters.

briefly and incompletely referred to, has received further experimental support during 1921. A careful scrutiny of all the absolute measurements of atomic-plane spacing and atomic distances in crystal structures, carried out up to the present by means of X-rays, has confirmed the first assumption that the atoms of each element, when regarded as spheres, possess the same diameter in all the crystallised compounds into which they enter, and that these constant atomic spherical dimensions are related, not as the valencies of the elements (the Pope and Barlow hypothesis), but in the manner graphically exhibited by the periodic curve reproduced from Prof. Bragg's memoir in Fig. 8. When the crystal is that of a chemical element the distance between the centres is actually the diameter of the sphere itself, the sum of the radii of the two equal spheres in contact; and when it is that of a chemical compound the distance

⁹ W. L. Bragg, *Phil. Mag.*, 1920, [vi], **40**, 169; *A.*, 1920, ii, 537.

separating the centres of two adjacent atoms of different elements is the sum of the two radii of the spheres, now different.

In all cases, in fact, the distance between the centres of contiguous atoms, whether of the same or different elements, is equal in absolute measure to the sum of the two atomic radii. These distances, moreover, correspond with the observed closest positions of the two elementary atoms, nearer than which they never approach, the limiting surface of each being apparently that of the outer shell of electrons, or at any rate that of a sphere of impenetrability, the atomic domain. A table of the actual values is next given, as derived from direct X-ray measurement with crystals, and it also includes the diameters of the atomic spheres of neon, argon, krypton, and xenon, derived from indirect determinations of the outer shells of electrons.

ATOMIC DIAMETERS, IN ÅNGSTRÖM UNITS.

$A. = 10^{-8}$ cm.

Atomic number.	Element.	Atomic diameter.	Atomic number.	Element.	Atomic diameter.
3	Lithium	3.00	26	Iron	2.80
4	Glucium	2.30	27	Cobalt	2.75
6	Carbon	1.54	28	Nickel	2.70
7	Nitrogen	1.30	29	Copper	2.75
8	Oxygen	1.30	30	Zinc	2.65
9	Fluorine	1.35	33	Arsenic	2.52
10	Neon	1.30	34	Selenium	2.35
11	Sodium	3.55	35	Bromine	2.38
12	Magnesium ...	2.85	36	Krypton	2.35
13	Aluminium ...	2.70	37	Rubidium	4.50
14	Silicon	2.35	38	Strontium	3.90
16	Sulphur	2.05	47	Silver	3.55
17	Chlorine	2.10	48	Cadmium	3.20
18	Argon	2.05	50	Tin	2.80
19	Potassium	4.15	51	Antimony	2.80
20	Calcium	3.40	52	Tellurium	2.65
22	Titanium	2.80	53	Iodine	2.80
24	Chromium	2.80	54	Xenon	2.70
	{(electro-} 2.35		55	Cæsium	4.75
	" {negative)} 2.35		56	Barium	4.20
25	Manganese	2.95	81	Thallium	4.50
	{(electro-} 2.35		82	Lead	3.80
	" {negative)} 2.35		83	Bismuth	2.96

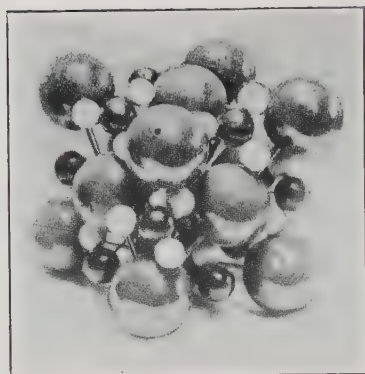
In making these comparisons from all the published material, and with the aid of new determinations of atomic diameters by Prof. Bragg himself, of which the results are expressed in the table, it has been clearly recognised that there are two very distinct types of structure in crystals, namely, (1) those in which the relative positions of all the atoms are fixed by the symmetry, and (2) those in which, while some atomic positions are fixed, those of other atoms are not but, within certain limits (usually along a line) which are dependent on the symmetry, are permitted some latitude of arrange-

ment, the exact positions being determinable by the *X*-ray measurements. The chlorides of sodium and potassium, zinc blende, and the diamond, are obviously of the first type; and iron pyrites of the second. For while the iron atoms in pyrites are fixed at the corners and face-centres of the cube, the sulphur atoms are situated on alternate diagonals, at a definite position on each of these diagonals which is not, however, fixed by the symmetry but has been found by *X*-ray measurement to be at the distance of 1.025 Å.U. from an unoccupied corner of the cubelet, eight of which cubelets form the main cube which has iron atoms at its corners and face-centres. Indeed, as there is another sulphur atom on the continuation of this same diagonal in each case, at the same distance from and on the other side of the unoccupied corner just referred to, the centres of these two sulphur atoms will be at the distance apart of 2.05 Å.U. Further, as sulphur atoms have never been found to approach closer than this, 2.05 Å.U. is the sum of the two radii and therefore the atomic diameter of sulphur.

The next striking fact brought out by the law of atomic diameters is that the electro-positive alkali metals, lithium, sodium, potassium, rubidium, and caesium stand out with remarkable prominence at sharp maxima of the curve, which is steep on each side of them; the alkaline earths follow some distance down, whilst the electro-negative elements and those dyad-acting metals which also form weak acidic oxides occupy the minima, which are much less sharp. That the size of the atomic sphere—be it sphere of influence or the outer spherical shell of electrons—is not a question of valency is quite clear. For the smallest atoms are those of oxygen of valency two and nitrogen of valency three or five, each having the atomic diameter 1.30 Å.U., whilst the univalent alkali metals have atomic domains varying from 3 to 4.75 Å.U., caesium, the most electro-positive element known, having this latter maximum atomic diameter. The atomic diameters are thus periodic functions of the atomic number. They will doubtless prove to be of great assistance in unravelling the structures of the more complex inorganic compounds.

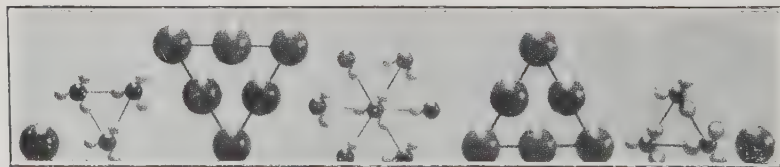
The Law of Atomic Diameters accords well with the Lewis-Langmuir version of the atomic structure theory; for the electro-negative elements which have the minima of atomic domain are precisely those which share electrons to complete the stable (inert gas) shell, having fewer electrons than correspond to the stable system. Indeed, it is apparently this sharing of electrons which causes the spheres to have smaller diameters than those of the electro-positive elements. On the other hand, as an electro-positive element does not share electrons in its outer shell with neighbouring

FIG. 9.



Model of Calcium Carbonate.

FIG. 10.



Dissected Model of Calcium Carbonate.

[To face p. 231.]

atoms, but has its active electron or electrons outside the stable shell, it occupies a greater space in the structure. Perhaps the most instructive case referred to by Prof. Bragg, as affording both types of attachment in the same chemical compound, is that of calcite, CaCO_3 , which is illustrated by models reproduced in Figs. 9 and 10, the latter showing the structure taken to pieces. The calcium atoms, represented by the large spheres, have each a double positive charge, whilst the carbon and oxygen atoms of the CO_3 group together afford a corresponding double negative charge; the carbon and oxygen atoms of this group share electrons and are consequently knitted closer together (approximately at their atomic radial distance), so their spheres are smaller as shown by the model, the smallest being the oxygen atoms (lightly shaded in the figure).

Important confirmatory evidence of the law has been brought forward by Prof. A. O. Rankine¹⁰ from the measurements of the viscosity of the four inert gases, and of oxygen, nitrogen, and the three halogens. He has found that the nearest approach of the atoms of any one of these gaseous or vaporised elements to each other during a collision is only slightly greater than the atomic diameter of Bragg. This is exactly what would be expected from thermally agitated atoms; a cushion or film of resiliency or repulsion between them (due probably to the electronic movements of Born and Landé) prevents absolute contact of the outer electronic shells on collision, otherwise attachment would occur. Prof. W. L. Bragg has pointed out, moreover, that both the viscosity and the crystal structure results point to the same increase in the size of the atom as each successive electron shell is added, there being a definite increase in the dimensions of the outer electron shell in passing from one period to the next.

The Law of Progressive Crystal Structure in Isomorphous Series containing the Alkali Metals.

The remarkable outstanding size of the atoms of the alkali metals, as so clearly shown by their sharp maxima in the curve of atomic diameters, and also the considerable progressive increase in the dimensions of their shells as we pass from one to another (belonging to successive periods), explain and render still more important the two most prominent facts emanating from the writer's researches on the crystal-characters of the isomorphous sulphate, selenate and double salt series $\text{R}_2\text{Se}^{\text{S}}\text{O}_4$ and $\text{R}_2\text{M}(\text{Se}^{\text{S}}\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$, in which R represents either potassium, rubidium, or cæsium. The first fact is that in the double salt series these alkali metals exert a vastly

¹⁰ A. O. Rankine, *Phil. Mag.*, 1920, [vi], **40**, 518; *A.*, 1920, ii, 679.

predominating influence in determining the properties of the crystals, their interchange causing a very definite change in the crystal angles and constants; whereas interchange of the dyad-acting M metals, which are near and almost on the minima of the curve of atomic diameters, has but a slight determinative effect on the angles, volume constants, and physical properties of the crystals. The second fact is that the specially marked changes due to interchange of the alkali metals, whether in the double salt series or in the alkali sulphates or selenates themselves, are definitely progressive, following the progression of the atomic numbers of the three alkali metals. Thus not only does the relatively very large size of the atoms of the three alkali metals (the cæsium atom being, as already mentioned, the largest of all atoms), and the consequent relative magnitude of the progressive difference in their sizes, cause the changes of crystallographic constants, both structural and physical, to be prominently marked, but it gives, in doing so, the maximum opportunity possible for any progressive character to reveal itself in these changes, corresponding to the addition of another electronic shell when we pass from potassium to rubidium and from the latter to cæsium. Hence, the choice of the salts of these metals—both the simple rhombic sulphates and selenates and the monoclinic hexahydrated double sulphates and double selenates—has proved a singularly suitable and fortunate one, and the Law of Progression of the Crystallographic Properties with Rise of Atomic Number of the Alkali Metals has been placed on the firmest possible basis.

Thus the Law of Atomic Diameters, together with the fundamental Law of Moseley—according to which the atomic number expresses the mass and positive charge on the atomic nucleus and also the number of the surrounding negative electrons—explains completely the results of the writer's investigations, which may be justly regarded as the natural consequence of these laws. Conversely also, Prof. Bragg may fairly consider that the writer's results support his law of atomic diameters.

It may perhaps be permitted to be stated in this Report, as the present moment marks the conclusion of a research which has occupied full thirty years, that the writer has now just completed the work on the last two groups of salts, the double selenates of the manganese and cadmium groups. Altogether seventy-five salts have been investigated, including also those in which R is ammonium and thallium, and also including a group of isomorphous double chromates, in investigating which the writer had the collaboration of Miss Mary W. Porter. The specially careful preparation of numerous crops of each of these seventy-five salts, the goniometry

of ten or more of the most perfect crystals of each of them, and the determination of their density (more than eight hundred crystals having been completely measured and five hundred density determinations carried out), the preparation of more than two thousand truly plane and correctly orientated surfaces with the very efficient aid of the cutting-and-grinding goniometer, in order to provide at least eight section-plates and six 60° -prisms of each substance, has alone been a formidable task, and fully explains the time over which the work has inevitably extended. It was felt to be essential to include every salt of these series which could be obtained in good crystals, and it is satisfactory to be able now to report that the conclusions are contributed unanimously, without any exception, by all the groups studied, which are nineteen in number. The crystal angles, the habits of the crystals, the volumes and edge-dimensions of the unit cells of the space-lattices, the dimensions and orientations of the optical ellipsoids, the molecular refraction constants, the thermal dilatations in all cases where it was possible to determine them, indeed the minutest details of the physical properties studied, have throughout exhibited the progression according to the atomic numbers of the three alkali metals ($K = 19$, $Rb = 37$, $Cs = 55$, a difference of eighteen at each step, corresponding to a whole Langmuir shell of electrons), the crystals of the rubidium salt invariably proving intermediate. The importance of the isostructure of the rubidium and ammonium salts, so clearly in all cases also revealed, has already been adequately referred to. In practically every property but refractive power, in which it is transcendently high, the thallium salt also stands close to the rubidium salt. It has been made very clear, moreover, that only the potassium, rubidium, and caesium salts are "eutropic" (following the law of progression with atomic number of alkali metal), the ammonium and thallium salts being only generally isomorphous. The largest amount of change of angle for any replacement of one R-base by another has proved to be $2^\circ 28'$ (between potassium copper and caesium copper selenates).

In two papers published during the year by Prof. P. Niggli of Zurich,¹¹ the editor of the now resuscitated *Zeitschrift für Kristallographie*, the connexion between crystal and atomic structure is discussed, and reference especially made to the writer's work. He points out that the homogeneity of crystal structure is not due to the arrangement of mere mass particles, but to the symmetry or structure of those particles themselves, the elementary atoms, and to the fields of force, orientated in character, which in consequence may be regarded as emanating from the atoms. He goes

¹¹ P. Niggli, *Z. Krist. Min.*, 1921, **56**, 12, 167; *A.*, 1922, ii, 36.

further in stating that from crystal structure that of the atoms building up the crystal ought to be elucidated. He turns largely to the determination of density in isomorphous series as an indication of the ranges, spheres of influence, or volumes of the atoms of the elements which by their mutual arrangement replace each other, and quotes the writer's determinations of the densities of the monoclinic hexahydrated series as typical and adequately accurate for his purpose, and as clearly proving the progressive growth of the sphere of influence of the atoms of the alkali metals as the atomic number increases. Niggli then analyses a considerable amount of the material in vols. I and II of Groth's "*Chemische Krystallographie*," with similar results, making allowances for less accurate experimental data, and finally arrives at relative volumes for the spheres of action of the atoms of many elements, and it is highly interesting that the corresponding relative diameters show the same regularities of periodicity as the atomic diameters in absolute measure of W. L. Bragg. This conclusion, moreover, was arrived at before the publication of Bragg's paper, so that it is doubly valuable as being an independent arrival at the Law of Atomic Diameters, largely from the work of the writer aided as far as possible by older measurements in other series, and especially confirmed as regards the morphological and volume constants by the excellent work of W. Muthmann on the permanganates and of T. V. Barker on the perchlorates of the alkalis.

In concluding this section of the Report, therefore, it may be pointed out how very satisfactorily the results of the investigations of so many different workers support, confirm, and amplify one another, so that we may now be sure that knowledge of real value and permanence has been arrived at during the year that has just closed.

Miscellaneous X-ray Results.

The Structure of Adularia and Moonstone.—The results of a useful investigation commenced at Cambridge by Mr. S. Kozu, concerning the structure of adularia and moonstone, and continued in Japan in collaboration with Y. Endo and M. Suzuki, are published in a new journal, *Science Reports of the Tohoku Imperial University, Sendai, Japan* (1921, Vol. I, No. 1, p. 1). Adularia and moonstone are supposed to be solid solutions of varying proportions of orthoclase, albite, and anorthite feldspars, moonstone being the variety of adularia which exhibits "schillerisation" (the display of a pearly, sub-metallic, or bronze-like lustre). The results indicate that adularia consists of a single space-lattice structure, a homogeneous solid solution, whilst moonstone has two different space-lattices of

like type, affording a double Laue radiogram, the two different substances being two kinds of solid solutions, both of monoclinic symmetry. On heating moonstone the two space-lattices approach each other and eventually become identical at 1060° , the lattice then being that of adularia. At about 1000° the schillerisation disappears. Hence this work has proved that schillerisation is not due to cavities and inclusions, as supposed, but to interference of ordinary light rays by the presence of two space-lattices alike in symmetry but quite distinct.

The Structure of "Liquid Crystals" has been studied by J. S. van der Lingen¹² by the Laue method of X-ray analysis, with the view of definitely testing whether these remarkable substances, so intimately associated with the name of Prof. Lehmann, are in reality endowed with a space-lattice structure, the criterion of a true crystal, as asserted by Vorländer, or are merely swarms of similarly orientated molecules, as supposed by Bose. *p*-Azoxyanisole, *p*-azoxyphenetole, anisaldazine, and active amyl cyanobenzylidene-aminocinnamate were produced in the so-called "liquid crystal" form in a strong magnetic field, and Laue X-radiograms taken of them. The result was definitely negative, no sign of a space-lattice being revealed. The regularity of structure producing double refraction and other optical effects simulative of crystals appears to be due merely to the similar orientation (parallelwise) of the flat elongated molecules themselves, the swarm theory of Bose being thus verified.

In a second memoir van der Linden¹³ describes further experiments with the anisotropic liquid (the liquid crystal) form of *p*-azoxyanisole, in which a pattern of faint horizontal lines was obtained, apparently due to diffraction from parallel layers of lamellar molecules, a direct confirmation, it would seem, of Bose's swarms. In the writer's opinion Prof. Lehmann is to be congratulated on this result, although it is not in conformity with his earlier views. For his "liquid crystals" thus become an intermediate stage, of deeper interest than ever, between true liquids and true crystals.

The Structure of Alabandite, MnS , has been studied by R. W. G. Wyckoff.¹⁴ The crystals belong to the hexakis tetrahedral class 31 of the cubic system, and X-ray analysis shows them to be constructed like rock-salt, but with some slight lack of symmetry in the lines of force about the atoms. It is thus different from zinc blende, ZnS . Magnesium oxide, MgO , afforded almost identical results, the sodium chloride structure being closely simulated.

¹² J. S. van der Lingen, *J. Franklin Inst.*, 1921, **191**, 651; *A.*, ii, 438.

¹³ *Loc. cit.*, **192**, 511; *A.*, ii, 681.

¹⁴ R. W. G. Wyckoff, *Amer. J. Sci.*, 1921, [v], **1**, 138; **2**, 239; *A.*, ii, 262, 700.

The Structure of the Ammonium Haloids has been investigated by Dr. Langmuir and G. Bartlett¹⁵ at different temperatures. The high-temperature form of each proves to be constructed like sodium chloride, each atom being surrounded by six others. The ordinary-temperature forms of the chloride and bromide possess a centred cube structure, each atom having eight others around it. It is considered that the ammonium "ion" has tetrahedral symmetry, while the alkali metals and halogens have cubic "ions."

Colloidal Substances.—An interesting X-ray investigation of so-called colloids has been carried out by Scherrer.¹⁶ Colloidal gold, the finest precipitated gold (that in the remarkable purple liquid which never deposits), was found to consist of minute crystal particles having the same face-centred cube structure as ordinary gold crystals, some of the particles being only 1.86×10^{-7} cm. in diameter, so that only five cube-lattice edge-lengths were contained in each particle. Colloidal silver also proved to be crystalline, with a face-centred cube lattice. Silica likewise proved to be crystalline, and the only true colloid among the substances examined was gelatin, which showed no sign of crystal structure.

Metallic Elements.—A. W. Hull¹⁷ has given a list during the year of further metallic elements investigated by him as regards their crystal structure by his powder method. The list is as follows, the dimensions of the cube edges or trigonal prism edges, and the axial ratio $a : c$ of the hexagonal metals, being also given.

Face-centred Cube Lattices.		Centred Cube Lattices.	
Calcium.....	5.56 Å.U.	Chromium	2.895 Å.U.
α -Cobalt	3.554 "	Molybdenum	3.143 "
Nickel	3.540 "	Tantalum	3.272 "
Rhodium	3.820 "	Hexagonal Close-packed Lattices. $a : c$	
Palladium	3.950 "		
Iridium	3.805 "	β -Cobalt	2.514 Å.U. 1 : 1.63
Platinum	3.930 "	Cadmium	2.960 " 1 : 1.89
		Ruthenium	2.686 " 1 : 1.59
		Zinc	2.670 " 1 : 1.86

The Structure of Ice has been studied by D. M. Dennison,¹⁸ by producing a shower of minute crystals in a water-filled capillary tube, plunging it into liquid air, and using the Hull method. The results indicate the close-packed hexagonal lattice, consisting of two sets of interpenetrating triangular prisms, with edges 4.52 Å.U. and height 7.32 Å.U. The axial ratio found was $a : c = 1 : 1.62$,

¹⁵ G. Bartlett and Irving Langmuir, *J. Amer. Chem. Soc.*, 1921, **43**, 84; A., ii, 261.

¹⁶ P. Scherrer, Zsigmondy's "Kolloidchemie," 3rd ed., p. 387.

¹⁷ A. W. Hull, *Physical Rev.*, 1921, **17**, 42, 571.

¹⁸ D. M. Dennison, *ibid.*, 1921, **16**, 20.

very near the theoretical 1.633 for a close-packed hexagonal arrangement of spheres. It may be remembered that Rinne found ice to be hexagonal bipyramidal, class 25 (that of apatite), with an axial ratio 1 : 1.678.

The Structure of the Silver Haloids has been determined by R. B. Wilsey,¹⁹ in the laboratory of the Eastman Kodak Company, Rochester, N.Y., also by the powder method. The precipitates obtained by adding potassium chloride, bromide, or iodide solution to a solution of silver nitrate were employed, and the results prove the crystalline character of these precipitated silver salts. Also powdered fused silver bromide was used, with identical results. The chloride and bromide are constructed of simple cube lattices of the side dimensions 2.78 and 2.89 Å.U. respectively, one atom being associated with each point of the lattice. Silver iodide, however, gave results which corresponded with the diamond lattice, each side of the cube being 6.53 Å.U., one atom being ascribed to each point of the structure; each iodine atom appears to be at the centre of a tetrahedron the corners of which are occupied by four silver atoms, and each silver atom is surrounded by four iodine atoms in the same manner, the distance of the atomic centres being 2.83 Å.U. The silver bromide and chloride precipitated in photographic emulsions form minute distinct cubic crystals; the iodide similarly produced in these emulsions appears to be hexagonal. These forms had not been studied, but a promise of such an investigation by X-rays is given. The result should be interesting, as silver iodide crystallises at the ordinary temperature in the dihexagonal pyramidal class 26 of the hexagonal system, and becomes converted on heating to 146° into a cubic form.

The Crystal-structure of Antimony and Bismuth.—Prof. A. Ogg²⁰ has confirmed the conclusion of James and Tunstall that the unit rhomb of each of these metals contains eight atoms. The edge of the unit rhomb of antimony is 6.20 Å.U., the structure consisting of two interpenetrating face-centred rhombohedral lattices, and the shortest distance between the atoms is 2.92 Å.U. James and Tunstall made it 2.87 Å.U. The length of the edge of the unit rhomb of bismuth was found to be 6.52 Å.U. R. W. James,²¹ in a further paper, gives it as 3.28 Å.U., the half of the value just quoted, and for the closest approach of two atomic centres 3.11 Å.U.

The Structure of Potassium Cyanide Crystals has been determined by P. A. Cooper²² with small single crystals, and found to resemble that of potassium bromide, the CN acting as a whole like Br. But

¹⁹ R. B. Wilsey, *Phil. Mag.*, 1921, [vi], 42, 262; *A.*, ii, 548.

²⁰ A. Ogg, *ibid.*, 163; *A.*, ii, 513. ²¹ R. W. James, *ibid.*, 193; *A.*, ii, 513.

²² P. A. Cooper, *Nature*, 1921, 107, 745.

no definite evidence was obtained as to the disposition of the atoms of carbon and nitrogen.

The Diamond.

Three papers of general interest concerning the diamond have appeared during the year 1921. One embodies a communication to the Mineralogical Society by Dr. J. R. Sutton,²³ Director of the Kimberley Observatory, S. Africa, who showed that diamond crystallises readily on garnet, iron pyrites, olivine, and ilmenite (FeTiO_3). These minerals are frequent inclusions in diamond, as are also graphite, bort, and diamond itself of unconformable orientation. So common are diamond inclusions (either fragments or complete crystals) in the diamonds found at Bullfontein that they impart a specific reputation to these "stones," for white spots, cross-grain, and "knots." It is these various inclusions which set up strain, and even fracture, in the enclosing diamond, and most diamonds found broken owe their rupture to this cause. Dr. Sutton entirely discredits the stories of bursting and exploding natural diamonds, and in a long experience has never known an authentic case. Such strain as there is in a diamond, revealed in the dark field of the polariscope, Dr. Sutton attributes entirely to inclusions, the thermal dilatation of which is different from that of the diamond. Artificial diamonds, however, do explode from strain. The late Sir William Crookes in his fascinating book "Diamonds" (page 120) describes how such an artificial diamond exploded on a microscope slide in his laboratory during the night, the diamond having been produced under great pressure.

A second paper by F. Fischer²⁴ deals with the artificial preparation of diamonds, and it is shown that under other than abnormally high pressures the separation of carbon as diamond (a non-conductor of electricity) can only occur below 700° , and that otherwise it appears as graphite (a conductor). The small size of the hitherto produced artificial diamonds he attributes to this fact, for at 700° the iron containing the carbon in solution has already solidified, so that the carbon could separate only in minute crystals. He suggests that larger diamonds would probably be produced if a substance could be found in which carbon is soluble and which is still molten at 700° .

The third paper concerns the compressibility of the diamond, which has been studied by L. H. Adams,²⁵ and found to be the lowest on record, namely, 0.16×10^{-6} per megabar (a megabar =

²³ J. R. Sutton, *Min. Mag.*, 1921, **19**, 208.

²⁴ F. Fischer, *Brennstoff-Chem.*, 1921, **2**, 9; *A.*, ii, 111.

²⁵ L. H. Adams, *J. Washington Acad. Sci.*, 1921, **11**, 45.

0.987 atmosphere), within the range of pressure from 4,000 to 10,000 megabars. The difference from graphite is immense, the value for graphite having been shown by Prof. T. W. Richards to be 3×10^{-6} , and that of steel to be 0.6×10^{-6} . Thus we have one more property added to those for which the diamond holds the record.

Concluding Remarks.

This Report has already reached the allotted span, and a number of other valuable contributions to the work of the year 1921 can only be mentioned. Dr. H. H. Thomas and Mr. A. F. Hallimond²⁶ have devised a useful direct-vision refractometer for liquids, which also serves the special purpose of preparing a liquid mixture of any required definite refractive index, a most desirable object in modern optical crystallography. Miss Mary W. Porter²⁷ has extended the research mentioned in the last Report, which she carried out in collaboration with Mr. T. V. Barker, by describing crystallographically a number of pyridine and picoline derivatives which might have been expected to show some morphotropic regularities. But organic radicle replacements prove to cause very great (indeed often entire) change of crystalline form, indicating how very sensitive crystal structure is to change of chemical composition.

Dr. Harold Hilton²⁸ has contributed two papers of mathematical and geometrical interest, one regarding the determination of optic axes from extinction angles, and the other concerning the vibrations of a crystalline medium. Both subjects are treated in a masterly manner, and the latter paper gives food for much thought, at a time when atomic structure is proving to be at the root of molecular movements and the building up of a crystal edifice. A new mineral, a basic copper phosphate, of peacock-blue colour by reflected light and greenish-blue by transmitted light, is described by Dr. A. Hutchinson (to whom hearty congratulations are due on his election as the new President of the Mineralogical Society) and Mr. A. M. Macgregor.²⁹ It proves to have the composition $2\text{Cu}_3(\text{PO}_4)_2 \cdot 7\text{Cu}(\text{OH})_2$, and was discovered in Northern Rhodesia.

Dr. L. J. Spencer³⁰ has published two papers. The earlier one deals with a substance which was described in the year 1879 by C. O. Trechman as an orthorhombic form of metallic tin and termed by him β -tin. It is now shown to be not tin but stannous sulphide,

²⁶ H. H. Thomas and A. F. Hallimond, *Min. Mag.*, 1921, **19**, 124.

²⁷ Miss Mary W. Porter, *T.*, 1921, **119**, 1769.

²⁸ H. Hilton, *Min. Mag.*, 1921, **19**, 233; *Phil. Mag.*, 1921, [vi], **42**, 148.

²⁹ A. Hutchinson and A. M. Macgregor, *Min. Mag.*, 1921, **19**, 225; *A.*, ii, 701.

³⁰ L. J. Spencer, *ibid.*, 113, 263; *A.*, ii, 266.

the orthorhombic crystals of which are often produced in tin smelting. Tin is thus not trimorphous, but only dimorphous, ordinary white tin being tetragonal, and "grey tin" (tin pest) cubic. The second memoir is a fascinating essay, with numerous beautiful illustrations, on curvature in crystals. Many of the most remarkable examples of curved crystals in the British Museum collection are described and portrayed. The paper is not only pleasantly readable, but forms an admirably concise summary of the types of crystal distortion and contortion.

To Dr. Spencer it is largely due that the new venture of the Mineralogical Society, the publication of *Mineralogical Abstracts*, commenced in March, 1920, has been carried successfully through eight numbers and is now so nearly up to date that nineteen of the memoirs published in the past year, 1921, have been dealt with. The value of these abstracts is now assured, and they are most heartily welcomed. To the December number of the *Mineralogical Magazine* Dr. Spencer also contributes a considerable number of valuable biographical notices, with portraits, of lately deceased crystallographers and mineralogists, including Profs. Fedorov, von Lang, and Voigt, together with an index to all such notices which have appeared in the *Magazine* since its inception in 1876.

In the March, 1921, number of the *Magazine* appears an important Report, of the Committee on British Petrographic Nomenclature, of which Committee, jointly appointed by the Geological and Mineralogical Societies, Prof. W. W. Watts was chairman and Lt.-Col. Campbell Smith was secretary. The recommendations will do much to bring order into the somewhat chaotic state of this nomenclature.

During the year 1921 the Mineralogical Society has lost one who was universally regarded as the "father" of the society, its president during the years 1885 to 1888 and its general secretary for the succeeding twenty-one years, Sir Lazarus Fletcher. His name is happily perpetuated in the "Fletcher Indicatrix," the ellipsoid now so conveniently used to express the optical properties of crystals. An admirable biographical notice by Sir Henry Miers, with portrait, appears in the June (1921) number of the *Mineralogical Magazine*, and in this same number, by a singular chance, is published also Sir Lazarus Fletcher's last paper, a memoir written with all his accustomed thoroughness, on "The Crumlin (Co. Antrim) Meteorite."

During the meeting of Science Masters at Oxford in January, 1921, some interesting demonstrations were given by Mr. T. V. Barker at the Mineralogical Department of the University, on "The Study of Crystals in Schools," and a very useful pamphlet

of "Practical Suggestions" for this study has been published by the Holywell Press.

During the year 1921 three important books have appeared. Of two bearing the same title, "Lehrbuch der Mineralogie," one is a new book by Prof. P. Niggli³¹ of Zurich, already referred to as the new editor of the resuscitated *Zeitschrift für Kristallographie*, and the other, edited by Prof. F. Becke³² of Vienna, is the 8th edition of the text-book of Prof. Gustav Tschermak. The third is a new book by Prof. P. von Groth,³³ an attempt to combine in abbreviated form the characters of his well-known "Physikalische Krystallographie" and of his large (5-volume) "Chemische Krystallographie."

By the time this Report appears it is probable that a second and very much enlarged edition of the writer's "Crystallography and Practical Crystal Measurement" will have been published. The immense amount of research, including the whole of the X-ray work, carried out since the appearance of the first edition in 1911, and the desirability of acceding to the many expressed wishes that the book should be made more fully to cover the whole subject, have caused it to be extended to two volumes.

It will be evident to all who read this Report how very considerably the crystallographic investigations of the past year, so large a proportion of which are British, have contributed to the very basis of Chemistry, the unravelling of the nature of the chemical atom. There is no longer any necessity for a crystallographer to plead for more attention to his subject, its value is now most clearly evident to all. The realm of Organic Chemistry is now also entered, and indeed no one can say how far the new methods of attack by X-rays will take us, the possibilities being immense. Perhaps, however, the most encouraging fact is that all this recent research has permanently confirmed the principles on which crystallographers of late years have built up their science. For, as the writer states in the preface to the new edition of his book, "not one single conclusion or principle, presented in the first edition, has been shown to be invalid or incorrect."

A. E. H. TUTTON.

³¹ P. Niggli, "Lehrbuch der Mineralogie," 1920, Gebrüder Borntraeger, Berlin.

³² G. Tschermak and F. Becke, *ibid.*, 8th edition, 1921, A. Hölder, Vienna and Leipzig.

³³ P. Groth, "Elemente der phys. und chem. Krystallographie," 1921, R. Oldenbourg, Munich and Berlin.

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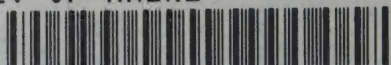
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